

[CONTRIBUTION FROM THE WILLIAM ALBERT NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

## The Stereochemistry of Complex Inorganic Compounds. XXII. Stereospecific Effects in Complex Ions<sup>1</sup>

BY E. J. COREY AND JOHN C. BAILAR, JR.

RECEIVED NOVEMBER 8, 1958

Stereospecific effects are observed in many of the reactions of complex ions which contain optically active coordinating agents. Some examples of such stereospecificity are described, and an explanation of them is given which depends on an analysis of the stereochemistry of individual chelate rings and of the relationship between the rings in bis- and tris-chelate complexes. For example, it is shown that the *dextro*- and *levo*-forms of  $[\text{Co en}_3]^{+3}$  can each exist in four conformational forms which differ in stability and which are in rapid equilibrium. One of these forms, designated herein as the "lel" form, is considerably more stable than the other three. The stereochemical requirements of the stable lel form are such that when a racemic 1,2-diamine is substituted for ethylenediamine all three ligands in the complex possess the same configuration. Hence, from a racemic 1,2-diamine, two isomers predominate at equilibrium,  $[\text{Co}(d\text{-amine})_3]^{+3}$  and its enantiomer  $[\text{Co}(l\text{-amine})_3]^{+3}$ . The approach which has been developed makes possible predictions of relative stabilities and reactivities of isomers and allows the assignment of absolute configuration to chelate compounds.

### I. Introduction

Studies of the stereochemistry of complex inorganic compounds have brought to light a considerable number of examples of stereospecificity. The phenomenon seems to be quite general, for the examples involve several different metals, and a wide variety of complexing agents, combined into both four covalent and six covalent complexes. In spite of the importance of the subject to our knowledge of stereochemistry, few systematic investigations have been made, and there has been no satisfactory explanation for the effects which have been observed. Jaeger<sup>2</sup> has attempted to relate the stability of diastereoisomers to the symmetry of the complex molecules, but his explanation does not account for the properties of the substances, even qualitatively. In this paper, some of the pertinent examples will be reviewed,<sup>3</sup> an analysis of the general stereochemistry of chelate compounds will be made and the results will then be applied to some of the examples which have been cited. Finally, the assignment of absolute configurations of chelate compounds will be discussed.

**II. Review of Experimental Data on Stereospecific Effects.**—Although the majority of the examples which have been described concern octahedral complexes in which the metal atom serves as a center of asymmetry, this is not a necessary condition for stereospecificity. For example, it has been found<sup>4</sup> that the tetracoördinate complex of palladium(II) with ethylenediaminetetraacetate is the optically active form (A) rather than the *meso* form (B). Repulsion between the uncoördinated carboxyl groups is doubtless an important factor, but other geometric influences may also play a part.

In a classic piece of work, Jaeger and Blumendal<sup>5</sup>

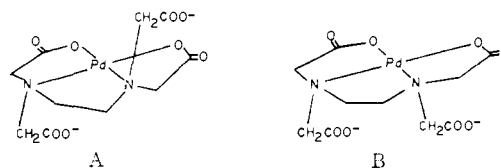
(1) Presented at a symposium on "The Mechanism of Inorganic Reactions in Solution," Evanston, Illinois, July 7, 1958. Some of the suggestions made in the discussion following that presentation have been considered in the body of this article. For these suggestions, the authors are indebted to Fred Basolo, Henry Freiser, G. M. Harris and J. V. Quagliano.

(2) F. M. Jaeger, *Proc. acad. Wetensch. Amsterdam*, **29**, 575 (1926); "Optical Activity and High Temperature Measurements," Cornell University Press, Ithaca, N. Y., 1930, Chapter 1X.

(3) For an earlier review, see J. C. Bailar, Jr., "Record of Chemical Progress," Winter Issue 1948, p. 17.

(4) D. H. Busch and John C. Bailar, Jr., *THIS JOURNAL*, **78**, 716 (1956).

(5) F. M. Jaeger and H. B. Blumendal, *Z. anorg. allgem. Chem.*, **175**, 161 (1928).



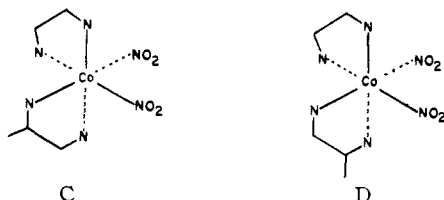
studied the stereochemistry of the cobalt(III) complexes containing the asymmetric base, *trans*-1,2-cyclopentanediamine. They observed that oxidation of a solution containing the *racemic* base and cobalt(II) ion leads to the formation of the isomers *trans*- $[\text{Co}(d\text{-cpn})_2\text{Cl}_2]^{+6}$  and *trans*- $[\text{Co}(l\text{-cpn})_2\text{Cl}_2]^{+6}$ , with no admixture of  $[\text{Co}(l\text{-cpn})(d\text{-cpn})\text{Cl}_2]^{+6}$ . When a solution of the *trans*-compound containing the *dextro* base, for example, was heated, conversion to the *cis*-form took place, the isomer *L*- $[\text{Co}(d\text{-cpn})_2\text{Cl}_2]^{+6}$  apparently being formed preferentially. This substance reacted readily with another mole of *dextro*-cyclopentanediamine to give *L*- $[\text{Co}(d\text{-cpn})_3]^{+3}$ , but when Jaeger and Blumendal tried to form  $[\text{Co}(d\text{-cpn})_2(l\text{-cpn})]^{+3}$  by the reaction of the *levo*-base with *L*- $[\text{Co}(d\text{-cpn})_2\text{Cl}_2]^{+6}$ , they obtained only a 2:1 mixture of *L*- $[\text{Co}(d\text{-cpn})_3]^{+3}$  and *D*- $[\text{Co}(l\text{-cpn})_3]^{+3}$ . The stereospecificity seems to be complete, for careful microscopic examination failed to indicate the presence of any of the other possible isomers.

Jaeger and Blumendal also observed some interesting effects in the formation of the complex  $[\text{Coen}_2\text{cpn}]^{+3}$ , which contains only one molecule of the optically active base. The reaction of the *racemic* complex *DL*-*cis*- $[\text{Coen}_2\text{Cl}_2]^{+6}$  with the *racemic* base, *dl*-cpn, is evidently completely stereospecific, for it gives only two products, *D*- $[\text{Coen}_2(l\text{-cpn})]^{+3}$  and *L*- $[\text{Coen}_2(d\text{-cpn})]^{+3}$ ; however, two products also were obtained from the reaction *DL*- $[\text{Coen}_2\text{Cl}_2]^{+6}$  and *l*-cpn. These were *D*- $[\text{Coen}_2(l\text{-cpn})]^{+3}$  and *L*- $[\text{Coen}_2(l\text{-cpn})]^{+3}$ . Unfortunately, Jaeger and Blumendal do not indicate the relative proportions in which these were formed, and they evidently made no attempt to determine whether

(6) The following symbols are used, representing in each case one mole of the coordinating agent: cpn, *trans*-1,2-cyclopentanediamine; en, ethylenediamine; tart, tartrate ion; pn, propylenediamine; i-bn, isobutylenediamine; 2,3-act-bn, 2,3-active-butylenediamine; m-bn, *meso*-butylenediamine; tetraMeen, 1,1,2,2-tetramethylethylenediamine; stien, stilbenediamine; trim, trimethylenediamine. The symbols *D* and *L* represent the signs of rotation of complexes at the *D*-line of sodium, and the symbols *d* and *l* the signs of rotation of ligand molecules.

one could be converted to the other. From the results of the experiment with the racemic base, it may be concluded that the *DL*-isomer is more stable than the *LL*, and that on heating the latter might change into the former.

The complexes of propylenediamine, in addition to showing isomerism based upon asymmetry of the octahedral structure and upon the asymmetry of the carbon atom, might be expected also to show an isomerism dependent upon the fact that the propylenediamine molecule is dissymmetric end for end. This has been designated as  $\alpha,\beta$ -isomerism; its actual existence was demonstrated by Werner<sup>7</sup> in his study of *cis*-[Co en (NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup>. Not only does this complex exist in *D*- and *L*-forms, and the propylenediamine in it in *d*- and *l*-modifications, but the methyl group may be adjacent to the equatorial plane containing the two nitro groups or distant from it. One pair of  $\alpha,\beta$ -isomers is represented by C and D.



Although there is nothing in Werner's paper to indicate that some of these isomers are more stable than others, it is probable that this is the case. The  $\alpha$ - and  $\beta$ -forms rotate the plane of polarized light by about the same amount, but the  $\alpha$ -forms crystallize in prisms, and the  $\beta$ -forms in needles. In view of such a striking difference, it is surprising that there is no evidence that a similar isomerism exists for [Co pn<sub>2</sub> X<sub>2</sub>], for [Co pn<sub>3</sub>]<sup>+</sup> or for [Pt-pn<sub>3</sub>]<sup>+</sup>.<sup>8</sup> It is not known whether some stereospecific influence forbids its existence in these cases or whether the isomers exist but are so similar in solubility that they have not been separated. Cooley<sup>9</sup> observed no stereospecific influences in the isolation of the *D* $\alpha$ , *D* $\beta$ , *L* $\alpha$  and *L* $\beta$  isomers of *cis*-[Co en ibn (NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup>, but Liu<sup>10</sup> found that the four isomers of *cis*-[Co en (2,3-act-bn)(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> are not of equal stability and that the less stable tend to rearrange to the more stable in solution. This evidence, and other relevant data, indicate that stereospecificity derives more from the presence of asymmetric centers in the ligands than from dissymmetry. However, the information on this point is too meager to allow the conclusion to be drawn with certainty.

In complexes containing two or three molecules of propylenediamine, stereospecific effects are very striking. Hurlimann<sup>11</sup> reported the preparation of *cis*-[Co(*d*-pn)(*l*-pn)(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup>, but there has been no other evidence, until very recently,<sup>12</sup> that molecules of both *dextro*- and *levo*-propylenediamine ever attach themselves to the same metal

atom. Smirnoff<sup>8</sup> reported that the reaction of racemic propylenediamine with platinum(IV) chloride gives only *D*-[Pt(*l*-pn)<sub>3</sub>]<sup>+</sup> and *L*-[Pt(*d*-pn)<sub>3</sub>]<sup>+</sup> and Tschugaeff and Sokoloff<sup>8</sup> observed that the reaction of [Co(*l*-pn)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> with *dextro*-propylenediamine gave a mixture of *L*-[Co(*l*-pn)<sub>3</sub>]<sup>+</sup> and *D*-[Co(*d*-pn)<sub>3</sub>]<sup>+</sup> rather than [Co(*l*-pn)<sub>2</sub>(*d*-pn)]<sup>+</sup>. The mixed complex may have been formed initially but disproportionated before it could be isolated. The complexes of platinum(IV) show much less tendency to rearrange than do those of cobalt(III), so one might hope to obtain mixed complexes by such reactions as *cis*-[Pt(*l*-pn)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> + *d*-pn → [Pt(*l*-pn)<sub>2</sub>(*d*-pn)]<sup>+</sup>. However, this experiment does not seem to have been tried. In any event, disproportionation reactions do not take place in every case, for both [Co(*l*-pn)<sub>2</sub>(*d*-tart)]<sup>+</sup> and [Co(*l*-pn)<sub>2</sub>(*l*-tart)]<sup>+</sup> can be obtained by the action of the appropriate isomer of tartaric acid on [Co(*l*-pn)<sub>2</sub>CO<sub>3</sub>]<sup>+</sup>. In these complex ions, the *d*-tartrate is held much more firmly than the *l*-tartrate, as is shown by the difference in rate of displacement of the tartrate by nitro groups<sup>13</sup> or by *levo*-propylenediamine.<sup>14</sup>

By careful fractionation of salts of the *tris*-*levo*-propylenediamine-cobalt(III) ion, Dwyer<sup>12</sup> has obtained both the *Llll* and the *Dlll* complexes, the former being generated in much greater quantity than the latter. In solution, the two isomers evidently exist in equilibrium, for upon heating, each was transformed into a mixture of the two.

Dwyer's observations on the complexes of optically active propylenediamine are in agreement with earlier observations on the behavior of [Co-*l*-pn<sub>2</sub>CO<sub>3</sub>]<sup>+</sup>. The *D*- and *L*-isomers of this ion were first prepared by Bailar and McReynolds<sup>15</sup> who described them as the "stable" and "unstable" forms because it was found that the latter, upon being heated in water solution, changed to the former. Later work<sup>16</sup> demonstrated, however, that the two forms are interconvertible. Evaporation of a solution of the material on the steam-bath gave a material showing a specific rotation (at the D-line of sodium) of +130°, whereas evaporation at room temperature yielded a product showing a rotation of -430°. Each of these, on standing in solution at room temperature, reverted to an equilibrium mixture.

Basolo, Chen and Murmann<sup>17</sup> have measured the formation constants of a series of copper(II) and nickel(II) complexes containing C-methylated ethylenediamines, and a portion of their results is shown in Table I.

It is seen that substitution of methyl groups into the ethylenediamine molecule has much less influence on the stabilities of the planar copper(II) complexes than on those of the octahedral nickel(II) ions. This is what might have been expected

(7) A. Werner, *Helv. Chim. Acta*, **1**, 5 (1918).

(8) L. T. Tschugaeff and W. Sokoloff, *Ber.*, **42**, 55 (1909); A. P. Smirnoff, *Helv. Chim. Acta*, **3**, 177 (1920).

(9) W. E. Cooley, Thesis, University of Illinois, 1954.

(10) C. F. Liu, Thesis, University of Illinois (1957).

(11) H. Hurlimann, Thesis, Zurich, 1918.

(12) F. P. Dwyer, private communication.

(13) Sister Mary Martinette, B.V.M., Thesis, University of Illinois, 1949.

(14) Hans B. Jonassen, J. C. Bailar, Jr., and E. H. Huffman, *THIS JOURNAL*, **70**, 756 (1948).

(15) John C. Bailar, Jr., and J. P. McReynolds, *ibid.*, **61**, 3190 (1939).

(16) Sister Mary Martinette, B.V.M., and J. C. Bailar, Jr., *ibid.*, **74**, 1054 (1952).

(17) F. Basolo, Yun Ti Chen and R. K. Murmann, *ibid.*, **76**, 956 (1954).

TABLE I  
FORMATION CONSTANTS OF COPPER(II) AND NICKEL(II)  
WITH C-SUBSTITUTED ETHYLENEDIAMINES

Complexing agent	$\log K_T (0^\circ)$ [Cu bases] <sup>++</sup>	$\log K_T (0^\circ)$ [Ni bases] <sup>++</sup>
en	21.29	20.05
pn	21.77	19.77
<i>d,l</i> -bn	22.87	20.39
<i>m</i> -bn	21.55	16.74
<i>i</i> -bn	21.19	15.98
tetraMeen	23.10	...
<i>d,l</i> -stien	21.23	19.61
<i>m</i> -stien	17.50	8.69 <sup>a</sup>

<sup>a</sup> The nickel complex of *meso*-stilbenediamine contains only two molecules of the base.

from the point of view of crowding of the coordinated groups, as will be considered in detail in a later section.

Cobalt(III) complexes containing stilbenediamine<sup>18</sup> differ from those containing propylenediamine in several aspects. Because of the aromatic rings in the base, the bis- and tris-stilbenediamine complexes are insoluble in water, but soluble in alcohol, and the experiments were performed in that solvent. Since the stilbenediamine molecule contains two similar asymmetric carbon atoms, it exists in a *meso*, as well as in optically active forms, and even though  $\alpha,\beta$ -isomerism does not exist, there are twenty possible isomers of the ion [Co stien<sub>3</sub>]<sup>+3</sup>. From the reaction of *trans*-[Co(*d*-stien)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> with *dextro*-stilbenediamine, Ferrone isolated both *D*-[Co(*d*-stien)<sub>3</sub>]<sup>+3</sup> and *L*-[Co(*d*-stien)<sub>3</sub>]<sup>+3</sup>; reaction of the same complex with *levo*- and *meso*-stilbenediamine gave evidence for the existence of both *D*- and *L*-[Co(*d*-stien)<sub>2</sub>(*l*-stien)]<sup>+3</sup> and both *D*- and *L*-[Co(*d*-stien)<sub>2</sub>(*m*-stien)]<sup>+3</sup>. Neither Ferrone nor Williams was able to prepare a complex containing three molecules of the *meso*-base.

There have been only a few studies of stereospecific effects in complexes which do not contain diamines. Lifschitz<sup>19</sup> prepared tris-*dextro*-alanine-cobalt(III), from which he separated two  $\alpha$ -forms, differing slightly in physical properties. From the shapes of the rotatory dispersion curves, Lifschitz concluded that these were the *ddd* and *lddd* isomers. He was not able to isolate the two  $\beta$ -forms from each other because of their much lower solubilities. The fact that the two  $\alpha$ -forms seem to be of similar stability provides evidence that stereospecific effects are not as great in the chelates of  $\alpha$ -amino acids as in diamine chelates of the same sized rings.

**III. General Stereochemical Analysis of Chelate Compounds and Applications.**—An understanding of the stereochemistry of metal chelates necessitates the solution of two distinct but related problems, (1) the orientation of donor atoms about the central metal ion and (2) the spatial arrangements which can be assumed by the individual chelate rings and their relative stabilities. The first of these is easily dealt with to a first ap-

proximation by assuming that in chelates the configuration of donor atoms around the metal ion is essentially the same as in the corresponding non-chelate complexes. However, this is only an approximation since some distortion from the regular orientation will result in cases where the normal angles between the metal-to-ligand bonds conflict with the geometrical requirements of the chelate ring.

The second aspect of the stereochemistry of metal chelates, which relates to the geometry of the chelate ring, is trivial for cases in which the chelate ring is rigid and planar (*e.g.*, acetylacetonate complexes) but assumes great significance when the rings are non-planar and flexible because of facile internal rotation. For these cases it is clear that stereospecificity will depend upon the spatial arrangement of the ring atoms and that the solution of stereochemical problems requires detailed consideration of ring geometry. For this reason, the stereochemistry of metal chelates ties in with the general subject of the stereochemistry of flexible cyclic structures. The techniques of stereochemical analysis which recently have achieved signal success when applied to flexible carbocyclic rings (*e.g.*, cyclohexane) are therefore relevant and it is this approach, frequently termed "conformational analysis,"<sup>20</sup> which dominates the stereochemical treatment of metal chelates outlined in the following sections. It is gratifying that this treatment is effective since it rests on quite basic principles of stereochemistry and, in consequence, unites the stereochemistry of metal chelates with that of purely organic structures.

**Geometry of Individual Chelate Rings.**—Attention is first directed to the five-membered chelate ring formed by ethylenediamine. This example is selected for consideration because it serves as an advantageous starting point for establishing the significance of ring geometry. The geometry of the five-membered metal-ethylenediamine chelate ring was calculated accurately by vector analysis by the method outlined earlier<sup>21</sup> using the normal values for the bond distances and four of the bond angles (the fifth bond angle is fixed by these data): C-C, 1.54 Å.; C-N, 1.47 Å., M-N, 2.00 Å. (M = metal); <MNC = <NCC = 109.5°. The results which were obtained are summarized in Table II,

TABLE II

Atom	Coördinates (x, y, z)	Ring angle
M	(-1.46, 0, 0)	86.2°
N <sub>1</sub>	(0, 1.37, 0)	109.5°
N <sub>2</sub>	(0, -1.37, 0)	109.5°
C <sub>1</sub>	(1.28, 0.74, 0.30)	109.5°
C <sub>2</sub>	(1.28, -0.74, -0.30)	109.5°
Ha*(N <sub>1</sub> )	(0.05, 1.85, -0.98)	...
He*(N <sub>1</sub> )	(-0.22, 2.14, 0.76)	...

which is based upon the model shown in Fig. 1. The N-M-N angle, calculated as 86.2°, is only slightly distorted from a right angle, which is the normal angle for regular octahedral and square planar complexes. The ring is markedly puck-

(18) O. F. Williams, Thesis, University of Illinois, 1951; B. A. Ferrone, Thesis, University of Illinois, 1957.

(19) J. Lifschitz, *Z. physik. Chem.*, **114**, 493 (1925).

(20) For a recent review, see D. H. R. Barton and R. C. Cookson, *Quart. Rev.*, **10**, 44 (1956).

(21) E. J. Corey and R. A. Snee, *THIS JOURNAL*, **77**, 2505 (1955).

ered<sup>22</sup> as is indicated by the  $z$  coordinates given in Table II and the fact that the angle between the projections of the two C-N bonds viewed down the C-C axis,  $\theta$ , is found to be  $48.8^\circ$  (for a planar ring



$\theta = 0^\circ$ ). These values, obtained by calculation using normal bond angles and bond distances, correspond to an essentially strain-free structure and agree almost exactly with those measured for  $[\text{Co en}_3]^{+3}$  by X-ray diffraction<sup>23</sup> [C-C, 1.54 Å.; C-N, 1.47 Å.; Co-N, 2.00 Å.;  $\angle \text{CoNC}$ ,  $109.5^\circ$ ;  $\angle \text{NCC}$ ,  $109.6^\circ$ ;  $\angle \text{NCoN}$ ,  $87.4^\circ$ ;  $\theta = 48^\circ$ ]. Consequently, there is no doubt that this geometry can be assumed for chelated ethylenediamine units in octahedral and square-planar complexes.<sup>24</sup> Alleviation of any slight NMN angle strain by increasing this angle toward  $90^\circ$  with compensating distortion of  $\angle \text{MNC}$  and/or  $\angle \text{NCC}$  would change ring geometry only slightly as is indicated by the data in Table III, based on a model with  $\angle \text{NMN} = 90^\circ$  and  $\angle \text{NCC} = 109.5^\circ$ .

TABLE III

Atom	Coordinates ( $x, y, z$ )	Ring angle
M	(-1.41, 0, 0)	$90^\circ$
N <sub>1</sub>	(0, 1.41, 0)	$104^\circ$
N <sub>2</sub>	(0, -1.41, 0)	$104^\circ$
C <sub>1</sub>	(1.23, 0.69, 0.35)	$109.5^\circ$
C <sub>2</sub>	(1.23, -0.69, -0.35)	$109.5^\circ$

An important feature of the chelate ring described in Table II is the fact that the hydrogen substituents on adjacent ring atoms are almost completely staggered, an arrangement which tends to minimize the energy of the cyclic structure as is apparent from data on carbocyclic systems, *e.g.*, cyclopentane and cyclohexane. Indeed, it is quite instructive to compare the geometry of chelated ethylenediamine with that of cyclohexane. The stable form of the cyclohexane ring is the chair form which is puckered in such a way as to allow the normal tetrahedral value for each ring angle and complete staggering of the hydrogens on adjacent carbon atoms. This form can be regarded as free of strain in comparison with other cycloparaffins and is more stable than the boat form (by *ca.* 5.6 kcal./mole) because the latter suffers from eclipsing and other repulsive interactions involving non-bonded hydrogens. In the chair form, the substituents are of two varieties, axial and equatorial, depending on whether the bond to carbon is parallel to the threefold symmetry axis through the center of the ring (axial bond) or extends outward from the center of the ring (equatorial bond). The angle  $\theta$  between the projection of any two alternate C-C bonds as viewed down the connect-

(22) J. V. Quagliano and S. Mizushima, *THIS JOURNAL*, **75**, 6084 (1953), have reported that infrared absorption data indicate puckering of chelated ethylenediamine rings with a *gauche* configuration for the ethylenediamine ligand.

(23) K. Nakatsu, M. Shiro, Y. Saito and H. Kuroya, *Bull. Chem. Soc. Japan*, **30**, 158 (1957).

(24) The metal-ethylenediamine ring in tetrahedral complexes is also puckered. In addition these chelate rings possess a considerable amount of angle strain.

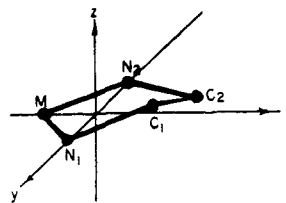
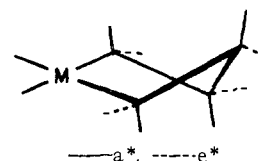


Fig. 1.—Metal-ethylenediamine ring as oriented for vector calculation.

ing C-C bond in chair-formed cyclohexane is  $60^\circ$ . The slightly smaller angle  $\theta$  in the metal-ethylenediamine cycle (*ca.*  $49^\circ$ ) indicates that the degree of puckering of the metal-ethylenediamine cycle is roughly comparable. Therefore, the substituents on a chelated ethylenediamine ring possess axial or equatorial character and can be regarded as axial type (abbreviated hereafter as axial\*) or equatorial type (equatorial\*). The puckered metal-ethylenediamine cycle may then be represented as

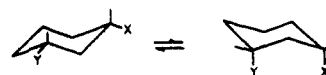


The substituents attached to carbon have about 80% axial or equatorial character; those attached to nitrogen have much less although they are still by no means equivalent.

In the case of cyclohexane the axial orientation is of higher energy than the equatorial orientation for groups larger than hydrogen, this difference increasing with the size of the substituent group (Table IV). The axial orientation of the group X involves compression with the *cis* axial substituents which increases with the size of X and which does not fall off as the C-X distance becomes larger, in contrast to the equatorial orientation.

TABLE IV

FREE ENERGY DIFFERENCES FOR THE CHANGE



Compound	Approx. $\Delta\Delta F$ (kcal./mole)	Ref.
X = Br, Y = OH	0.6	25
X = OH, Y = H	0.8	26
X = CH <sub>3</sub> , Y = H	1.8	26, 28
X = CH <sub>3</sub> , Y = OH	3.3	27
X = CH <sub>3</sub> , Y = CH <sub>3</sub>	>5	28

The same considerations apply qualitatively to the axial\* and the equatorial\* orientations in the ethylenediamine chelate ring. In the case of an octahedral complex the difference in free energy for a given group on carbon,  $\Delta F_{a^*} - \Delta F_{e^*}$ , is probably considerably greater than for the same groups in the cyclohexane series because of the

(25) E. L. Eliel and R. G. Haber, *Chemistry & Industry*, 264 (1958).

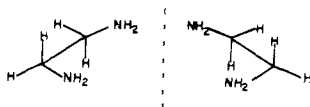
(26) S. Winstein and N. J. Holness, *THIS JOURNAL*, **77**, 5582 (1955).

(27) E. L. Eliel and C. A. Lukach, *ibid.*, **79**, 5986 (1957).

(28) C. W. Beckett, K. S. Pitzer and R. Spitzer, *ibid.*, **69**, 2488 (1947).

large axial groups on the metal. The  $\Delta F_{a^*} - \Delta F_{e^*}$  difference is probably also enhanced for an ethylenediamine ring in a tetrahedral metal complex. However, in the case of a carbon substituent on the ethylenediamine rings of square planar complexes  $\Delta F_{a^*} - \Delta F_{e^*}$  should be less than the corresponding value for a cyclohexane derivative due to the somewhat smaller degree of puckering. These conclusions are critically important to the stereochemical analysis of metal chelates with ligands such as ethylenediamine, as will become apparent from the illustrations which follow.

The chair form of cyclohexane can be converted to another (equivalent) structure by internal rotation and in a similar way the skew form of the metal-ethylenediamine ring can be changed to a skew form which is a reflection (mirror image) of the original. As a result of this process axial bonds are transformed into equatorial bonds and *vice versa*. The two reflectionally related skew forms of the metal-ethylenediamine cycle correspond to the two reflectionally related forms of *gauche* ethylenediamine and are designated herein as *k* and *k'* configurations.



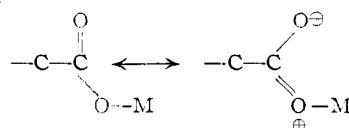
Another five-membered chelate system of interest is the cycle resulting from coordination of an  $\alpha$ -amino acid with a metal ion. Assuming normal bond distances and angles (with  $\angle \text{O-CO-C} = 120^\circ$ ) the degree of puckering which the ring must adopt is considerably less than in the ethylenediamine chelate ring. Since there is a strong tendency toward coplanarity of the ring members for maximum bonding, especially with respect to the O-CO bond, it seems advisable to consider the ring as being approximately planar. For this as well as for other reasons the distinction between substituents in the axial-equatorial sense is completely inappropriate (see Part II).

An approach to stereochemical problems involving rings of other sizes can be based on similar considerations. Chelate rings containing less than five members are expected to be considerably strained, and it is not surprising that these are less common. However, little information is available regarding the geometry of such rings.

With six-membered chelates, non-planar rings are frequently encountered. When the angle N-M-N is equal to  $90^\circ$ , as it is in octahedral and square planar structures, the chelate ring derived from trimethylenediamine is free of angle strain. However, for an M-N distance of *ca.* 2 Å., or more, it is forced into a more sharply folded conformation than that of cyclohexane. The chair-formed rings which are possible can be expected to be much more stable than the various possible boat forms. For a given ring in an octahedral complex, there are two such chair forms (not necessarily energetically equivalent because of interactions with the adjacent ligands), and these possess substituents which are essentially (but not strictly) of the axial-equatorial type. As a result of the enhanced puckering of the

six-membered chelate ring, the interactions between *cis*-axial substituents are intensified since the corresponding bonds are forced in toward one another. In addition, the interaction between adjacent equatorial groups is increased slightly because these substituents are less well staggered than in cyclohexane. Thus, substantial destabilization of this particular ring system relative to the metal-ethylenediamine cycle should be anticipated due to compression and eclipsing interactions, and the magnitude of this effect will be especially large when bulky axial groups are present. In octahedral complexes, for example, one of the axial positions on the metal-trimethylenediamine cycle must be occupied by a relatively bulky donor group; and, consequently, considerable destabilization results.

The six-membered ring derived from  $\beta$ -amino acids contains three fewer substituents than that from trimethylenediamine and repulsions involving substituents will, therefore, be less serious. However, the coplanarity requirement forced upon the ring for maximum electron delocalization, especially of the type



necessitates considerable angle strain and for this reason these chelate rings are not as stable as those formed from  $\alpha$ -amino acids.<sup>29</sup>

It is obvious that the above considerations do not pertain to those planar, fully conjugated, six-membered rings (*e.g.*, those derived from anions of 1,3-dicarbonyl compounds) which represent quite favorable electronic arrangements and which are comparable in stability to aromatic systems. However, these ideas can be extended to other non-planar ring systems which possess axes of internal rotation, including the larger rings. In such cases, the analogy between metal chelates and cycloparaffins is clearly useful. The instability of seven and eight-membered chelate rings, for example, can be attributed at least in part to the same factors which destabilize cycloheptane and cyclooctane relative to cyclohexane, *viz.*, compression and eclipsing interactions, which also can be considered as a type of internal entropy effect. Formation of chelate rings by coordination is favored relative to formation of non-cyclic complexes by a less negative translational entropy change.<sup>30</sup> However, this factor can be outweighed by adverse internal entropy effects in the case of the larger rings.

**Geometrical Relationships between Chelate Rings.**—It is also advantageous to focus on the specific case of the metal-ethylenediamine cycle to illustrate the factors which influence the relationship between chelate rings about a metal ion. As mentioned above, an *isolated* metal-ethylenediamine ring may adopt either of two configurations which are energetically and geometrically equivalent.

(29) See (a) "Stability Constants of Metal-ion Complexes," part I, Metcalfe and Cooper Ltd., London, E. C. 2, 1957; and (b) J. C. Bailar, Jr., "The Chemistry of Coordination Compounds," Reinhold Publ. Corp., New York, N. Y., 1956, p. 39.

(30) See A. W. Adamson, *THIS JOURNAL*, **76**, 1578 (1954).

lent but which are enantiomeric, designated as  $k$  and  $k'$ . In a system containing more than one ring, even with a fixed orientation of the donor nitrogens, the ethylenediamine ligands may, in principle, be arrayed about the metal ion in a number of ways since each ring may possess either the  $k$  or  $k'$  configuration. Although the energy barrier separating these structures is probably small,<sup>31</sup> the various forms can be expected to differ in thermodynamic stability, possibly to the extent that one form will predominate. In general, differences in potential energy (or free energy) between such conformational forms arise from the non-bonded interactions involving the groups attached to the metal (*i.e.*, donor groups). As in the case of all spiro rings, these groups are simultaneously members of one ring and substituents on another. Such interactions are now considered for the square-planar, tetrahedral and octahedral metal chelates.

For a square-planar arrangement of two ethylenediamine chelate rings there are three possibilities: the enantiomeric and energetically equivalent  $kk$  and  $k'k'$  structures and a  $kk'$  structure (identical with the  $k'k$  structure) as illustrated in Fig. 2. The relative free energies of these two forms in solution will depend on differences in the interactions between non-bonded atoms in each structure and differences in solvation. The energy difference exclusive of solvation effects can be calculated for the  $kk$  and  $kk'$  forms using the hydrogen-hydrogen potential function of Mason and Kreevoy,<sup>32</sup> since the only significant differences between the two forms are the hydrogen-hydrogen interactions of the adjacent  $\text{NH}_2$  groups of opposite rings. Although such a calculation does not yield the desired energy difference precisely, it does provide evidence for the order of stability. The energy difference,  $E_{kk'} - E_{kk}$ , thus calculated is approximately 1 kcal./mole, which implies that at equilibrium at room temperature the  $kk$  form will predominate over the  $kk'$  form by a factor of *ca.* 5. There is no simple way of calculating the difference in solvation energies of the  $kk$  and  $kk'$  forms at present, and so it cannot be regarded as certain that the  $kk$  form will predominate in solution. However, it seems probable that the difference in solvation energies of the two forms is essentially negligible because the charge distribution and accessibility to solvent are virtually identical in the two forms.<sup>33</sup>

The important difference between the  $kk$  and  $kk'$  arrangements for two square-planar ligands can

(31) The interconversion process,  $k \rightleftharpoons k'$ , simply involves rotation about internal, single-bond axes of the metal-ethylenediamine cycle. The barrier for this process is undoubtedly too low to give rise to classical stereoisomerism (*cf.*, ref. 22) since the intermediate structures are only slightly strained. There is again an analogy with the cyclohexane system in which chair-chair and chair-boat interconversions occur with low (<10 kcal./mole) activation energy.

(32) E. A. Mason and M. M. Kreevoy, *THIS JOURNAL*, **77**, 5808 (1955). The distances between the hydrogens of the *cis*- $\text{NH}_2$  groups of different rings, the only distances required for our calculations, were obtained by vector analysis and are as follows: (1)  $kk$  form— $d(\text{H}_{\text{ax}}-\text{H}_{\text{ax}})$  3.60 Å.,  $d(\text{H}_{\text{eq}}-\text{H}_{\text{eq}})$  2.91 Å.,  $d(\text{H}_{\text{eq}}-\text{H}_{\text{ax}})$  2.77 Å.; (2)  $kk'$  form— $d(\text{H}_{\text{ax}}-\text{H}_{\text{ax}})$  3.02 Å.,  $d(\text{H}_{\text{eq}}-\text{H}_{\text{eq}})$  2.48 Å.,  $d(\text{H}_{\text{eq}}-\text{H}_{\text{ax}})$  3.27 Å.

(33) X-Ray evidence indicates that in the crystalline state, *trans*- $[\text{Co}(\text{en})_2\text{Cl}_2] \cdot \text{HCl} \cdot 2\text{H}_2\text{O}$  possesses the  $kk'$  arrangement of chelate rings [A. Nakahara, Y. Saito and H. Kuroya, *Bull. Chem. Soc., Japan*, **25**, 331 (1952)]. Since our analysis predicts that the  $kk$  form of this sub-

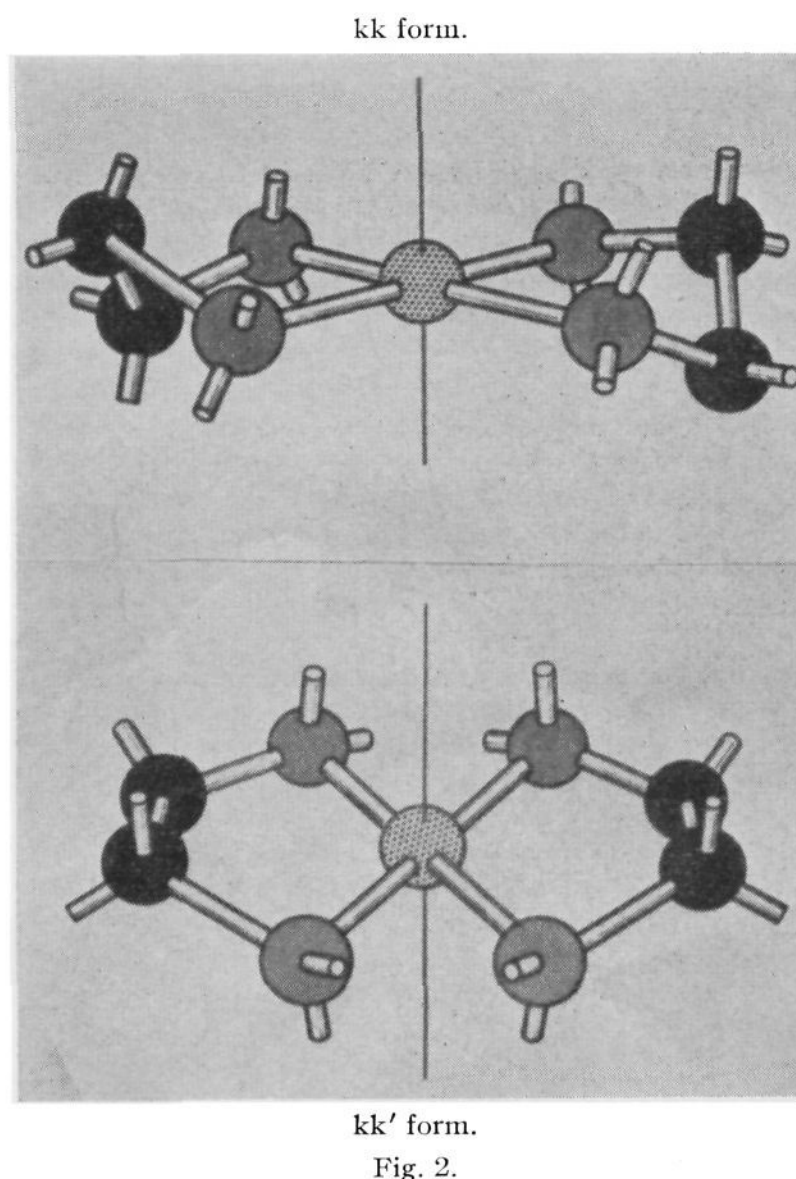


Fig. 2.

be seen clearly in Fig. 2: the hydrogens attached to the donor nitrogens of different rings are directly opposed in the  $kk'$  form but are staggered, and hence further removed from one another, in the  $kk$  and  $k'k'$  structures.

In the case of a tetrahedral bis-ethylenediamine chelate the  $kk$  and  $k'k'$  configurations are again enantiomeric and probably more stable than the  $kk'$  ( $= k'k$ ) configuration. In the  $kk'$  configuration each axial\*  $\text{N}-\text{H}$  is opposed to a neighboring equatorial\*  $\text{N}-\text{H}$  on the other ring (*i.e.*, the nitrogens and hydrogens of the two  $\text{N}-\text{H}$  groups are coplanar) making a total of four repulsive non-bonded interactions, whereas in the  $kk$  configuration there are only two such interactions which involve only the equatorial\*  $\text{N}-\text{H}$  units. The difference in stability between the  $kk$  and  $kk'$  forms in the tetrahedral complex is roughly of the same order of magnitude as for the square-planar variety, although it is probably somewhat greater.

Perhaps the most interesting cases, however, are the octahedral tris-ethylenediamine complexes for which, with a given configuration about the metal, four different forms are possible,  $kkk$ ,  $k'kk$ ,  $k'k'k$  and  $k'k'k'$ . These four structures generally all have different free energies and, of course, the order of stability is exactly reversed if the configuration about the metal is inverted. Calculation of the relative potential energies of these forms is more complex than that for the case

stance will be more stable intrinsically than the  $kk'$  form, we propose that in this case the  $kk'$  form must be favored by specific intermolecular forces in the solid state.

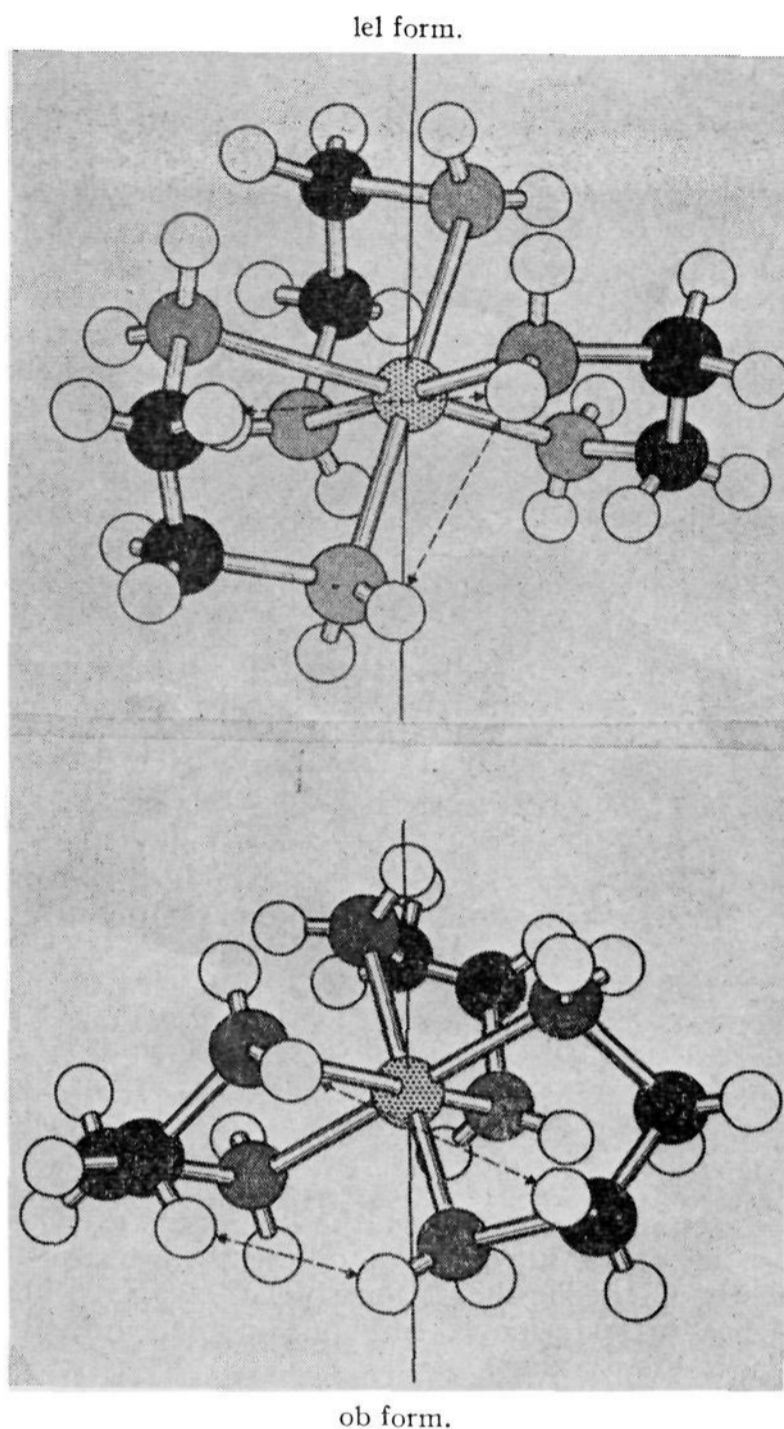


Fig. 3.

of two chelate rings with the square-planar orientation for three reasons: (1) a larger number of hydrogen-hydrogen interactions must be evaluated, (2) hydrogen-carbon interactions between the two carbons of a ring and the hydrogens of the axial  $\text{NH}_2$  groups must be evaluated and (3) electrostatic (inverse square) interactions between the hydrogens of the donor  $\text{NH}_2$  groups must be considered. This calculation has been carried out for the two extreme forms,  $\text{kkk}$  and  $\text{k}'\text{k}'\text{k}'$ , having the same configuration of rings about the asymmetric metal. Evaluation of the hydrogen-hydrogen and carbon-hydrogen interactions by the method of Kreevoy and Mason leads to the result that one of the forms, arbitrarily taken as the  $\text{kkk}$  form for this discussion, is more stable than the other by *ca.* 1.8 kcal./mole. The  $\text{kkk}$  form is favored mainly because of the less severe hydrogen-carbon interactions, which were calculated conservatively assuming the same potential function for carbon-hydrogen as for hydrogen-hydrogen interactions. It should be emphasized that the calculated energy difference for this complicated case is only a rough approximation which has little quantitative significance. However, the conclusion regarding the

order of stability should be valid because of the conservative treatment of the carbon-hydrogen interactions. The difference in electrostatic (inverse square) interactions between the  $\text{NH}_2$  groups in the two forms is negligible. It seems reasonable that the difference in solvation energy for these two forms will be less than the above value for the difference in internal energy because the shapes are so similar.

It is desirable to designate these two types of complexes which are shown in Fig. 3, in a descriptive way. The carbon-carbon bonds of the stable  $\text{kkk}$  complex are approximately parallel to the short trigonal axis  $aa'$ , whereas in the unstable  $\text{k}'\text{k}'\text{k}'$  complex the carbon-carbon bonds are slanted obliquely relative to the short trigonal axis. Consequently, the stable complex is designated herein as the "lel" form and the unstable complex as the "ob" form.

The  $\text{kkk}'$  and  $\text{kk}'\text{k}'$  forms possess energies intermediate between the  $\text{kkk}$  and  $\text{k}'\text{k}'\text{k}'$  extremes and the stability sequence predicted for the set is simply  $\text{kkk} > \text{kkk}' > \text{kk}'\text{k}' > \text{k}'\text{k}'\text{k}'$  for a given metal configuration. It would appear from our analysis that detectable amounts of the  $\text{kkk}'$  and  $\text{kk}'\text{k}'$  forms might be present at equilibrium but no estimate can be made regarding quantities.

The above illustrations, based upon ethylenediamine chelates, indicate the types of interactions which affect the relationship between chelate rings. The sections which follow deal with the application of these ideas to specific problems.

**Illustrations.**—The stereospecific effects observed with the bis-(*trans*-1,2-cyclopentanediamine) complexes<sup>5</sup> (see Part II), for which heretofore there has been no satisfactory interpretation, can be explained simply and unambiguously on the basis of the stereochemical factors detailed above. The N-C-C-N chain in these compounds possesses a fixed, skew configuration of the gauche ethylenediamine type and each enantiomer can form chelate rings of only one configuration, say  $k$  for the *d*-isomer and  $k'$  for the *l*-isomer. The enantiomers correspond to  $\text{kk}$  and  $\text{k}'\text{k}'$  forms and the internally compensated isomer corresponds to the  $\text{kk}'$  form. Because the difference in energy between the  $\text{kk}$  and  $\text{kk}'$  forms here should be essentially the same as for square-planar forms ( $E_{\text{kk}'} - E_{\text{kk}} \approx 1$  kcal./mole), it follows that  $[\text{Co}(\text{d-cpn-l-cpn})\text{Cl}_2]^+$  will be the less stable isomer in the *trans* series and will account for only a small part of the equilibrium mixture at room temperature. This is in accord with the results observed by Jaeger and Blumendal.<sup>5</sup>

The stereospecificity observed in octahedral complexes containing three molecules of *trans*-1,2-cyclopentanediamine also can be rationalized. The synthesis of chelates derived from the racemic diamine and cobalt(III) or rhodium(III) ions produces only  $\text{D-}[\text{M}(\text{l-cpn})_3]^{+3}$  and  $\text{L-}[\text{M}(\text{d-cpn})_3]^{+3}$ ; no appreciable amounts of the other six possible isomers have been isolated. These enantiomeric products undoubtedly are equilibrium controlled. The dextro-rotatory complex can be designated as  $\text{D-}[\text{M}(\text{kkk})]^{+3}$  and, following the generalization given above, this will be the lel form and will be more stable than the other possibilities, *e.g.*,  $\text{D-}[\text{M}(\text{k}'\text{k}'\text{k}')]^{+3}$  or  $\text{D-}[\text{M}(\text{k}'\text{k}'\text{k}')]^{+3}$  (ob) forms. In the case of

the levorotatory complex, the isomer  $L-[M(k'k'k')]$  (1el) will be the most stable. The  $k$  used here corresponds to the configuration of the rings derived from *levo*-cyclopentanediamine and the  $k'$  corresponds to rings derived from *dextro*-cyclopentanediamine. The high degree of stereospecificity which has been reported would indicate that our calculated energy difference between *ob* and *1el* forms is too small.

The occurrence of similar stereospecificity in complex formation between propylenediamine and metals is also subject to straightforward interpretation. The most stable complexes of cobalt(III) with this diamine are the enantiomeric  $D-[Co(d-pn)_3]^{+3}$  and  $L-[Co(l-pn)_3]^{+3}$  forms. Similarly, in the case of the platinum(IV) complex, the  $L-[Pt(d-pn)_3]^{+4}$  and  $D-[Pt(l-pn)_3]^{+4}$  complexes are the most stable. Although propylenediamine can, in principle, form both  $k$  and  $k'$  type chelate rings, these are not of equal energy since the methyl group must be axial\* in one and equatorial\* in the other. This energy difference, probably in excess of 2 kcal. per mole for octahedral complexes, is sufficient to ensure the formation of mostly  $k$  units (say) from *dextro*-propylenediamine and  $k'$  units from *levo*-propylenediamine. Since the most stable octahedral complexes are the *1el* type with the same configuration for all three ligand rings, all three propylenediamine units will be *levo*- for one configuration about the metal and *dextro* for the opposite configuration. In summary, the most stable cobalt(III) tris-propylenediamine complex is that in which all of the chelate rings about a given cobalt possess the same configuration with the methyl substituent equatorial\*; this necessitates that all three ligands be either *d-pn* or *l-pn*. The formation of  $D-[Co(d-pn)_2(l-pn)]^{+3}$  and  $L-[Co(l-pn)_2(d-pn)]^{+3}$  in minor proportion is not unexpected.

In actuality, further possibilities for isomerism exist since propylenediamine ligands can form  $k$  configuration rings with methyl equatorial in two different ways. Two different geometrical isomers result for each of the enantiomeric sets of  $[Co(pn)_3]^{+3}$  complexes which correspond to the " $\alpha$ " and " $\beta$ " isomers of Werner. These can also be described as *cis* (two equivalent forms) or *trans* (six equivalent forms), and statistically these would be expected to occur in the ratio one to three. As mentioned earlier, data on the occurrence of these geometrical isomers are lacking in the case of bis- and tris-propylenediamine complexes.

NOTE ADDED MARCH 9, 1959.—F. P. Dwyer, F. J. Garvan and A. Shulman, THIS JOURNAL, **81**, 290 (1959), have reported the formation from *d*-propylenediamine of a new cobalt complex in addition to the previously described major isomer  $D-[Co(d-pn)_3]^{+3}$ . This has been formulated as  $L-[Co(d-pn)_3]^{+3}$ , although, as is stated, the two substances might, instead, be geometrical ( $\alpha, \beta$ ) isomers. At equilibrium (20°)  $D-[Co(d-pn)_3]^{+3}$  predominates over the new isomer by a factor of 5.75.

Stereochemical analysis of chelate rings also provides an insight regarding the stability of chelate complexes as can be illustrated by a few examples. The total formation constants for nickel(II) tris complexes expressed in Table I are particularly interesting. The values of  $K_T$  for *en*, *pn* and *d,l*-*bn* are within a factor of 10 of one

another but are greater by *ca.*  $10^4$  than those for *m-bn* and *i-bn*. The large difference in stability correlates nicely with the fact that whereas in the former group, which are more stable, all the methyl groups may occupy the equatorial\* orientation, in the latter group half of the methyl groups necessarily possess the axial\* orientation. Similarly, the complex of nickel(II) with *d,l*-stilbenediamine (in which all phenyl groups are equatorial\*) is more stable than the *meso*-stilbenediamine complex (in which half the phenyl groups must be axial\*) by *ca.*  $10^{11}$ . These destabilizing effects must be caused mainly by the interaction between the large axial\* group and the *cis* axial donor  $NH_2$  group since they disappear in the case of the square-planar copper(II) complexes.

In the section on ring geometry it was concluded that five-membered chelates from 1,2-diamines should generally be more stable than the corresponding six-membered chelates from 1,3-diamines because the latter are subject to unfavorable internal entropy effects due to a highly folded conformation. It is desirable to cite here some of the experimental evidence on this point. Table V, which presents data on the stability constants of the copper(II) and nickel(II)-ethylenediamine and trimethylenediamine complexes, illustrates a number of points. First, the six-membered ring is generally less stable than the five-membered ring and this difference, measured by the quantity  $\log K^5 - \log K^6 (= \Delta \log K)$ , for a given metal increases as ligands are added to the central ion. The increase in  $\Delta \log K$  values in going from  $K_1$  to  $K_2$  is an indication that the donor  $NH_2$  groups of different rings interact more seriously in the case of the six- than the five-membered ring.<sup>34</sup> The inherent instability of a single chelated six-membered ring as compared to that of a five-membered ring is measured roughly by the  $\Delta \log K_1$  values and amounts to 1.25 kcal./mole. The difference in free energy of interaction between donor groups of different rings for the five- *vs.* the six-membered rings can be estimated for square planar structures from the quantity  $(\Delta \log K_1 - \Delta \log K_2)$  for copper(II) and is also approximately 1.25 kcal./mole.

As mentioned in the discussion of six-membered ring geometry, the octahedral complexes formed from trimethylenediamine should be greatly destabilized by the inescapable presence of an axial  $NH_2$  group on each of the highly puckered chelate rings, so it is not surprising that the  $\Delta \log K_3$  value for the nickel complex is quite large. The same considerations lead to the conclusion that in solution in the energetically more favorable form of the nickel(II)-bis-diamine complexes, the four donor atoms and the metal lie in the same plane. This is indicated by the similar values for  $\Delta \log K_1$  and  $\Delta \log K_2$  for copper and nickel.

The observation that the tetrachloro-1,2,3-triaminopropane-platinate(IV) chelate and the dichloro-platinate(II) chelate possess the five-membered ring structures rather than the alternative six-membered chelate structures emphasizes further the relative stability of the five-membered

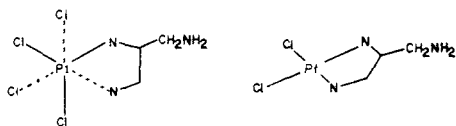
(34) The same conclusion is reached by calculation of hydrogen-hydrogen interactions.



TABLE V  
FORMATION CONSTANTS OF COPPER(II) AND NICKEL(II) WITH ETHYLENEDIAMINE AND TRIMETHYLENEDIAMINE (AT 0° IN 0.15 M KNO<sub>3</sub>)<sup>35a</sup>

Reagents	log K <sub>1</sub>	log K <sub>2</sub>	log K <sub>3</sub>	log K <sub>T</sub>
Cu(II), en	11.45	9.83	..	21.28
Cu(II), trim	10.52	7.94	..	18.46
	Δ log K <sub>1</sub> 0.93	Δ log K <sub>2</sub> 1.89	..	Δ log K <sub>T</sub> 2.82
Ni(II), en	7.88	6.70	4.78	19.36
Ni(II), trim	6.98	4.93	1.90	13.81
	Δ log K <sub>1</sub> 0.90	Δ log K <sub>2</sub> 1.77	Δ log K <sub>3</sub> 2.88	Δ log K <sub>T</sub> 5.55

rings.<sup>35</sup> In these instances the five-membered rings should possess considerably higher rotational entropy than the rigid chair-formed six-membered rings due to the possibility of side chain (-CH<sub>2</sub>-NH<sub>2</sub>) rotation and should be favored further for this reason.

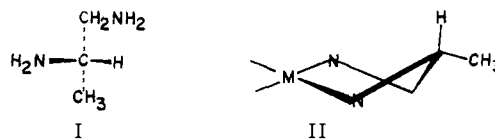


Recently O'Brien and Toole<sup>36</sup> have measured the optical rotatory dispersion of a number of complex ions containing optically active diamines and have found that the rotatory dispersion is independent of the nature of the metal ion with certain metals. They have interpreted these data in terms of a complete lack of stereospecificity in the coordination of these metals (e.g., zinc, cadmium and platinum(IV)) with asymmetric diamines. However, their conclusions are subject to serious question because of the fact that none of the metals studied absorbs light appreciably at the wave lengths used in the measurements. Under these circumstances an asymmetrically substituted metal need not necessarily contribute to rotatory dispersion of the complex in the spectral range covered by the experiments.

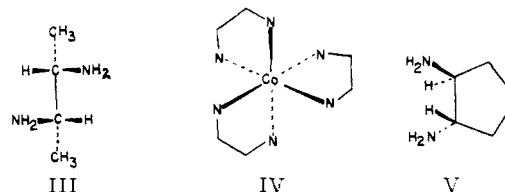
**IV. Assignment of Absolute Configuration of Chelate Complexes.**—The principles of stereochemical analysis developed herein can also be applied to the determination of the absolute configuration of an asymmetrically substituted metal ion. Such an application depends only on a knowledge of the relative orientation of the various groups in a metal complex and a knowledge of the absolute configuration of one of the ligand groups.

The method can be illustrated by derivation of the absolute configuration of D-[Co(*d*-pn)<sub>3</sub>]<sup>+3</sup> and its enantiomer. Considering the dextro complex formed from *d*-propylenediamine, each chelate ring will possess the same configuration and more specifically that in which the methyl substituent possesses the equatorial orientation. Since *d*-propylenediamine has been related to natural L-alanine by modification of COOH in the latter to CH<sub>2</sub>NH<sub>2</sub> of the former,<sup>37</sup> it must possess the absolute configuration shown by I and the absolute configuration of *d*-propylenediamine chelate rings must be that shown in II. With three ligand rings

of configuration II, two diastereomeric octahedral complexes are possible; these differ in the configuration of ligand groups about the metal and correspond to the unstable *ob* type complex and the stable *lel* complex (Fig. 3). Since the relative orientations of all groups in the stable *lel* complex



are clear and since the absolute configuration of the *d*-propylenediamine ligand is known, the absolute configuration of the whole complex is defined. The configuration around cobalt in D-[Co(*d*-pn)<sub>3</sub>]<sup>+3</sup> deduced in this way is represented by III.



Since optical rotatory dispersion curves for D-[Co(*d*-pn)<sub>3</sub>]<sup>+3</sup> and D-[Co(en)<sub>3</sub>]<sup>+3</sup> correspond,<sup>38</sup> III must also represent the absolute configuration of the latter. This result agrees with the absolute configuration found for D-[Co en<sub>3</sub>]<sup>+3</sup> by X-ray analysis.<sup>38</sup>

It is of interest that the stable form of [Pt(*d*-pn)<sub>3</sub>]<sup>+4</sup> is the levorotatory form, indicating that the platinum and cobalt complexes of the same absolute configuration differ in sign of rotation (sodium-D line). However, the dextrorotatory complex with rhodium(III) corresponds in configuration to D-[Co en<sub>3</sub>]<sup>+3</sup>.

From the absolute configuration of D-[Co(*d*-pn)<sub>3</sub>]<sup>+3</sup> and the fact that the stable form of [Co(*l*-cpn)<sub>3</sub>]<sup>+3</sup> is dextrorotatory, it follows that the absolute configuration of 1-*trans*-1,2-cyclopentanediamine is as indicated by IV. This prediction has not been checked at present and, to our knowledge, no other evidence has been obtained regarding the absolute configuration of 1-*trans*-1,2-cyclopentanediamine.

The dextrorotatory form of 2,3-butylenediamine has been assigned<sup>39</sup> the configuration shown by V.

(35) F. G. Maun, *J. Chem. Soc.*, 1224 (1927); 890 (1928).

(36) T. D. O'Brien and R. C. Toole, *THIS JOURNAL*, **77**, 1368 (1955).

(37) H. Reihlen, K. Weinbrenner and G. V. Hessling, *Ann.*, **494**, 143 (1932).

(38) Y. Saito, K. Nakatsu, M. Skiro and H. Kuroya, *Bull. Chem. Soc. Japan*, **30**, 795 (1957).

(39) F. H. Dickey, W. Fickett and H. J. Lucas, *THIS JOURNAL*, **74**, 914 (1952).

Assuming that this assignment is valid, it follows from the above considerations that the stable trischelate of *d*-2,3-butylenediamine with cobalt(III) will be dextrorotatory at the D-line of sodium.

It is hoped that the method for correlation of absolute configurations which has been illustrated above will prove reliable and useful.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE UNIVERSITY OF CONNECTICUT]

## The Preparation of Some Ternary Oxides of the Platinum Metals<sup>1,2</sup>

BY JOHN J. RANDALL AND ROLAND WARD

RECEIVED DECEMBER 4, 1958

Ternary oxides of the alkaline earth ions with ruthenium, rhodium, iridium and platinum have been prepared.  $\text{CaRuO}_3$  and  $\text{SrRuO}_3$  and  $\text{SrIr}_{0.5}\text{Ru}_{0.5}\text{O}_3$  are orthorhombic substances of the perovskite type.  $\text{BaRuO}_3$  has a hexagonal structure.  $\text{Sr}_2\text{RuO}_4$ ,  $\text{Sr}_2\text{RhO}_4$  are isotypic with  $\text{Sr}_2\text{IrO}_4$  which has the  $\text{K}_2\text{NiF}_4$  structure.  $\text{Sr}_4\text{IrO}_8$ ,  $\text{Sr}_4\text{PtO}_8$  and an oxygen-deficient  $\text{Sr}_4\text{RhO}_{8-\gamma}$  were found to have the  $\text{K}_4\text{CdCl}_6$  structure. Preliminary data suggest that  $\text{Sr}_3\text{Pt}_2\text{O}_7$  is structurally related to  $\text{Ba}_3\text{Pt}_2\text{O}_7$  and that ruthenium and iridium form ternary oxides with lead which have the pyrochlorite structure.

While there are many ternary oxides of transition metals, relatively few of these contain a platinum metal. Waser and McClanahan<sup>3</sup> have prepared a phase, at first formulated as  $\text{NaPt}_3\text{O}_4$  and later as  $\text{Na}_2\text{Pt}_3\text{O}_4$ . The presence of square  $\text{PtO}_4$  groups in this preparation was ascertained by a structure determination. The existence of this phase later was confirmed by Scheer, Van Arkel and Heyding,<sup>4</sup> who have prepared the analogous palladium compound. These authors also have prepared the compounds  $\text{LiRhO}_3$ ,  $\text{Li}_2\text{RhO}_3$ ,  $\text{NaRhO}_2$ ,  $\text{Na}_2\text{IrO}_3$ ,  $\text{Na}_2\text{PtO}_3$ ,  $\text{Li}_2\text{PtO}_3$  and  $\text{Li}_2\text{PtO}_3$  in which the platinum metal is in sixfold coordination with oxygen.

Ternary oxides of alkaline earth cations and platinum metals which have been reported are  $\text{Ba}_3\text{Pt}_2\text{O}_7$ <sup>5,6</sup> and  $\text{SrIrO}_4$ .<sup>7</sup>

The quaternary oxides  $\text{BaTi}_{0.75}\text{Pt}_{0.25}\text{O}_3$  and  $\text{Ba}_4\text{Ti}_2\text{PtO}_{10}$  also have been described.<sup>8</sup> The former is isotypic with hexagonal barium titanate.

An example of a ternary oxide of a lanthanide element and a platinum metal has been found in  $\text{LaRhO}_3$ <sup>9</sup> which has the orthorhombic modification of the perovskite structure typified by  $\text{GdFeO}_3$ .<sup>10</sup>

This paper describes the preparation and characterization of a number of ternary oxides of the types  $\text{ABO}_3$ ,  $\text{A}_2\text{BO}_4$  and  $\text{A}_4\text{BO}_6$ , where A represents Ca, Sr or Ba and B represents Ru, Rh, Ir or Pt.

### Experimental

**General Method of Preparation.**—For products prepared in air, the reactants were usually the alkaline earth carbonate and the platinum metal powder (~200 mesh). Reactants were ground thoroughly in an agate mortar and the mixture was fired in powder form, in air, at 1000 to 1500°. With the

exception of the rhodium preparation, the reactions took place rapidly, and a pure product could be obtained in several hours with two intermediate grindings of the reaction mixture.

For the preparations made *in vacuo*, the reaction mixture, in pellet form, was sealed in an evacuated silica capsule.

The ruthenium products were blue-black in color, the rhodium and iridium preparations were black, while the platinum compounds were tan or brown.

**ABO<sub>3</sub> Type Compounds.**—The reaction of ruthenium metal with alkaline earth carbonates at 1200° for periods of 12 to 24 hr. gave homogeneous dark blue products. The X-ray powder pattern of the calcium and strontium compounds were interpreted by analogy with patterns of other known compounds. Thus the calcium ruthenium oxide was found to resemble closely  $\text{CaMoO}_3$ <sup>11</sup> which probably has the orthorhombic structure of the  $\text{GdFeO}_3$  type.<sup>10</sup> The strontium ruthenium oxide on the other hand showed a strong resemblance to  $\text{LaVO}_3$ ,<sup>12</sup> which has been indexed with a tetragonal cell. A number of "split" lines, however, are observed in the pattern of the strontium ruthenium oxide. On the assumption that the two lines of the first "split" (corresponding to the 404 reflection for the tetragonal cell) were the 404 and 044 reflections of an orthorhombic unit cell the entire pattern could be indexed. The lattice constants for calcium ruthenium oxide were  $a = 5.53 \text{ \AA}$ ,  $b = 5.36 \text{ \AA}$ ,  $c = 7.67 \text{ \AA}$ , and for the strontium compound  $a = 5.57 \text{ \AA}$ ,  $b = 5.53 \text{ \AA}$ ,  $c = 7.85 \text{ \AA}$ . The barium compound appeared to be quite different. The X-ray powder pattern was indexed on the basis of a hexagonal unit cell  $a = 9.95 \text{ \AA}$ ,  $c = 21.54 \text{ \AA}$ .<sup>13</sup>

In view of the fact that a perovskite-type compound was not obtained in the strontium-iridium-oxygen system,<sup>7</sup> an attempt was made to substitute iridium for ruthenium in the strontium ruthenium oxide. Homogeneous products were obtained in the system  $\text{SrIr}_x\text{Ru}_{(1-x)}\text{O}_3$  between the limits  $0 < x < 0.5$ . In the region  $0.5 < x < 1.0$ , mixtures of  $\text{SrIr}_{0.5}\text{Ru}_{0.5}\text{O}_3$ ,  $\text{Sr}_2\text{IrO}_4$  and metallic iridium were formed. All the phases between  $0 < x < 0.5$  were orthorhombic and the lattice constants at  $x = 0.5$  were  $a = 5.58 \text{ \AA}$ ,  $b = 5.55 \text{ \AA}$ ,  $c = 7.84 \text{ \AA}$ . It was not found possible to substitute any platinum for the ruthenium in this phase.

The composition of these phases is not precisely known. The A/B cation ratio is probably near unity. Attempts to prepare phases in the systems  $\text{SrRu}_x\text{Ir}_{1-x}\text{Ru}_{1-x}\text{IV}\text{O}_{3-x/2}$  and  $\text{Sr}_{1-x}\text{Ru}_x\text{Ir}_{1-x}\text{IV}\text{O}_3$  were fruitless. Heterogeneous products were always obtained and the lattice dimensions for the orthorhombic phase remained unchanged. Approximate measurements of conductivities of the alkaline earth ruthenium oxide phases using pressed pellets sintered at 1200° gave values of about one reciprocal ohm cm. Direct oxygen

(1) Taken in part from a Doctoral Thesis submitted by John J. Randall, Jr., to the Graduate School of The University of Connecticut.

(2) This research was supported in part by the Office of Naval Research. Reproduction in whole or in part is permitted for any purpose of the United States Government.

(3) J. Waser and E. McClanahan, *J. Chem. Phys.*, **19**, 40, 413 (1951).

(4) J. Scheer, A. Van Arkel and R. Heyding, *Can. J. Chem.*, **33**, 683 (1955).

(5) M. G. Rousseau, *Compt. rend.*, **109**, 144 (1889).

(6) W. O. Statton, *J. Chem. Phys.*, **19**, 40 (1951).

(7) J. J. Randall, Jr., L. Katz and R. Ward, *THIS JOURNAL*, **79**, 266 (1957).

(8) H. Blattner, H. Gränicher, W. Känzig and W. Merz, *Helv. Phys. Acta*, **21**, 341 (1948).

(9) A. Wold, B. Post and E. Banks, *THIS JOURNAL*, **79**, 6365 (1957).

(10) S. Geller and E. A. Wood, *Acta Cryst.*, **9**, 563 (1956).

(11) W. H. McCarroll, L. Katz and R. Ward, *THIS JOURNAL*, **79**, 5410 (1957).

(12) M. Kestigian, J. G. Dickinson and R. Ward, *ibid.*, **79**, 5598 (1957).

(13) The indexing of this pattern has been filed with the microfilm service.