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STRUCTURE, REACTIVITY, SPECTRA, AND REDOX PROPERTIES OF COBALT(III) HEXAAMINES

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I. Introduction

A. Scope

Since the early days of coordination chemistry, cobalt amine complexes have played a dominant role. The classical work of Werner and

Jörgensen (*1*) is based on this class of compounds. Throughout the eventful historical development they were and still are key compounds in such diverse study areas as synthesis, coordination geometry and isomerism, spectroscopy (optical and NMR), conformational analysis, stability, substitution kinetics and mechanism, and redox processes. The overall coordination chemistry of cobalt has been reviewed in "Comprehensive Coordination Chemistry" (*2*). That review, however, does not deal with ammonia and aliphatic amine ligands. In a general way these important ligands are introduced in one of the introductory systematic chapters in the series (*3*). The last previous comprehensive review dealing with cobalt amine complexes was published in 1974 as part of Gmelin's handbook. An updated synoptic coverage of this part of coordination chemistry appears appropriate. It would be an impossible task, however, to exhaustively review the chemistry of cobalt amine complexes. Some arbitrary and personally biased choices have been made. First, we consider only those coordination compounds having a complete CoN_6 core, thus excluding the enormous number of CoN_{6}-xLx complexes. Second, to keep the volume of this chapter within manageable limits, for the authors as well as prospective readers, only ammonia and organic amines with an aliphatic skeleton are considered. Imines and heterocyclic nitrogen donors such a pyridine, bipyridine, and the plethora of their derivatives are not included. Third, this chapter is restricted to complexes containing just one kind of ligand, that is, homoleptic complexes.

Another set of arbitarily chosen boundary conditions concerns the list of physical and chemical properties that are summarized or discussed. The areas under consideration concern structural properties and their relationship to kinetic stability (toward hydrolysis and racemization), electronic structure, reduction potentials, and electron transfer processes.

Terminology

In this chapter the generic term amine will be used to describe any (potential) amine ligand including ammonia; the term ammine will be used solely to mean coordinated ammonia. Wherever possible we have used the most common abbreviations for the ligands.

B. SYNTHETIC ROUTES TO COBALT AMINE COMPLEXES

As a rule, rather simple and straightforward preparative procedures yield coordination complexes of cobalt with donors such as NH_3, en, and many other ligands. Whereas cobalt(III) complexes are typically very robust and air-stable, the corresponding cobalt(II) complexes are not only substitution labile, exchanging ligands on the microsecond time scale (*4*) in some cases, but most are easily oxidized by oxygen.

The standard preparative procedure for the Co(III)–amine complexes consists of the reaction of an aqueous or alcoholic solution of a Co(II) salt with the free base of the amine. Oxidation in the solution is achieved by air, oxygen, H_2O_2, or other oxidants. To prevent the reaction from stopping at the tetra- or penta-amine stage, especially with monodentate ligands, a surface-active catalyst, usually charcoal, is added to produce good yields of the Co(III)–N_6 species. Numerous variations of this classical procedure have been developed and optimized for each particular complex. See for example the series "Inorganic Syntheses." Intermediates in autooxidation of these amine complexes are interesting μ-peroxo bridged dimer complexes with a rich chemistry of their own (*5*). Several procedures where the cobalt starting material is already in oxidation state III have been described; typical starting materials in those cases are $[Co(CO_3)_3]^{3-}$, *trans*-$[Co(Cl)_2(pyridine)_4]^+$ and $[Co(NH_3)_5Cl]^{2+}$. A special situation relates of course to the cage complexes described by Sargeson and co-workers, where the bi-cyclic structure is built in situ from a $[Co(en)_3]^{3+}$ base (*6, 7*).

Strictly anaerobic conditions combined with a considerable excess of ligand are required for the synthesis of Co(II)–hexaamine complexes. A large excess of ligand must be used as a consequence of the characteristically high substitution rate at the center and competition for coordination sites by the solvent. In contrast to their counterparts in oxidation state III, the Co(II) amines are quite delicate compounds, the study of which often requires elaborate techniques and exclusion of air.

C. MOLECULAR MECHANICS

In this chapter the term molecular mechanics will describe a method used frequently to predict structures and relative energies of related complexes (usually isomers). The method involves summing the potential energy of all the interatomic interactions in terms of bond deformation, valence angle deformation, torsion angle deformation, and nonbonded interactions. The total potential energy of a particular arrangement of atoms is then given by

$$E_{\text{tot}} = \Sigma E_{\text{b}} + \Sigma E_{\theta} + \Sigma E_{\phi} + \Sigma E_{\text{nb}} \qquad (1)$$

The positions of the constituent atoms are varied to minimize U_{tot}. The precise formulas, force fields, and minimization techniques employed differ from author to author. The force field is defined as the collection of constants and equations that govern the energy of the interactions. The force fields employed are generally obtained by fitting to best reproduce observed physical properties, most often structures observed in the solid state, although spectroscopic force constants were the origin of all the force fields. Several relatively recent reviews on the application of molecular mechanics to coordination chemistry have appeared (*8*, *9*, *10*). The technique can be quite useful in coordination chemistry, particularly at predicting structures of complex ions and the relative stability of conformers and isomers for Co(III) hexaamine complexes. It should be noted however that the calculated structures do not include solvation effects, which can be large, and many comparisons are made with crystal structures where crystal packing forces can be important.

II. Structure of Cobalt Hexaamine Complexes

Numerical data obtained from X-ray crystallographic analysis on the structure of many of the complexes discussed in this section are listed in Table I.

A. MONODENTATE LIGANDS

1. *Ammonia* (NH_3)

The simplest complex in this review is the $[Co(NH_3)_6]^{3+}$ ion. In the Co(III) state the mean Co–N bond length is 1.960(6) Å (in the $[Hg(CN)_5]^{2-}$ salt) (*11*). The complex in the solid state is slightly distorted from an octahedral array of ligating atoms by crystal packing forces. The cobaltous ion has mean Co–N bond lengths of 2.183(2) Å (PF_6^- salt) (*12*) and 2.160(5) Å (Cl^- salt) (*13*).

2. *Methylamine* (NH_2Me)

The structure of the hexakis complex of this ligand has only very recently been determined (*14*). The complex is distorted in the solid state in a manner suggestive of repulsive forces between the methyl groups of one ligand with the nitrogen atom of another, Co–N–C angles of ~120°. The mean Co–N bond length is significantly longer than for the hexaamine complex at 2.013 Å.

3. *Hydroxylamine* (NH_2OH)

The structure of the hexakis complex of NH_2OH has also been reported recently (*14*). In contrast to the methylamine complex the mean

Co–N bond length is similar to that of the hexaamine complex at 1.958 Å, despite the greater steric hindrance due to the hydroxo group as compared to a proton.

B. BIDENTATE LIGANDS

1. Five-membered Rings

Tris bidentate complexes containing 5-membered rings, in addition to overall configurational isomerism (Λ or Δ, Fig. 1), exhibit conformational isomerism; that is, the chelate rings are not planar but adopt a skew (sometimes referred to as *gauche*) conformation. Individual chelate rings may adopt one of two conformations, *lel* or *ob*. This notation is defined by the line between the atoms that are bonded directly to the ligating atoms (in this case the two methylene carbons in the ring), being either almost paral-*lel* or *ob*-lique to the (pseudo) threefold axis of the complex (Fig. 1). This nomenclature system is an extension of proposals by Corey and Bailer (*15*). The IUPAC (*16*) nomenclature for this type of conformational isomerism is based on a system of skew lines: The line joining the ligating atoms defines the axis of a helix; another line joining the two atoms bound to the ligating atoms in the chelate defines a segment of a helix that has either left- or right-handed character. If the skew lines define a right-handed helix the conformation of the ring is designated δ; with the opposite sense, λ (see Fig. 2). Both these nomenclature systems have merit; each will be used when it most conveniently describes the situation. For example the *lel*/*ob* system is invariant with absolute configuration of the complex [e.g., a Λ(*lel*$_3$) complex is enantiomeric to a Δ(*lel*$_3$), but Λ(δ$_3$) is enantiomeric with Δ(λ$_3$)]. The λ/δ nomenclature is convenient in some cases because many asymmetric ligands adopt only one or the other of the δ/λ conformations. The relationship between the two designations is quite simple. When the overall configuration of the complex is Δ, the *lel* conformation is λ and the *ob* conformation is δ; vice versa for the Λ configuration [e.g., Δ−λλλ = Δ(*lel*$_3$), Λ−δλλ = Λ(*lelob*$_2$)].

a. 1,2-ethanediamine (en). For $[\mathrm{Co(en)_3}]^{3+}$, the ligand conformational changes are rapid in solution, and there is an equilibrium between the various possible isomers, *lel*$_3$, *lel*$_2$*ob*, *lelob*$_2$ and *ob*$_3$. Estimates of the distribution of $[\mathrm{Co(en)_3}]^{3+}$ between the four possible conformers have been made both by molecular mechanics calculations (*17*) and by analysis of NMR data (*18, 19, 20, 21*). Molecular mechanics predicts that the *lel*$_3$ conformer is more stable than the *lel*$_2$*ob* by ~2.7 kJ mol^{-1} and that *lelob*$_2$ and *ob*$_3$ have almost equal strain energies, about

TABLE I

Structural Data for Cobalt (III) and Cobalt (II)[a] Complexes

Complex	Co–N (Å)	Chelate bite angle (degrees)[b]	Trigonal twist, ϕ^c (degrees)	Reference
$[CO(NH_3)_6]^{3+}$	1.960(6)[d]			(*11*)
$[Co(en)_3]^{3+}$ *lel*$_3$	1.964(3)	85.5	55.0	(*25,26*)
lel$_2$*ob*	1.96(2)	86(1)	55.2	(*27, 28*)
lelob$_2$	1.964(4)	84.5	54.3	(*29,30,31*)
fac-$[Co(R\text{-}pn)_3]^{3+}$ *lel*$_3$	1.975(6)	85.9(2)	54.1	(*43*)
fac-$[Co(R\text{-}pn)_3]^{3+}$ *ob*$_3$	1.971(4)	84.2(1)	54.1	(*44*)
$[Co((\pm)-2,3\text{-}bn)_3]^{3+}$ *lel*$_3$	1.958(2)	85.0	53.6	(*228*)
mer-$[Co(ibn)_3]^{3+}$	1.98(2)	84.5		(*52*)
$[Co(tmen)_3]^{3+}$ ob$_3$	1.999(6)	80.0	43.9	(*53*)
$[Co(chxn)_3]^{3+}$ lel$_3$	2.02(3)	86.7(10)	53.4	(*229*)
ob$_3$	1.980(3)	84.1(1)	50.6	(*230*)
lel$_2$ob	1.972(5)	84.5(2)	53.7	(*231*)
$[Co(SS\text{-}cptn)_3]^{3+}$ *lel*$_3$	2.00(2)	87.0(5)	54.2	(*60*)
$[Co(SS\text{-}dpen)_3]^{3+}$	1.99(3)	83.5(8)	51.4	(*65*)
$[Co(tn)_3]^{3+}$ *chair*$_3$	1.98(1)	90.4(1)	59.8	(*70*)
$[Co(RR\text{-}ptn)_3]^{3+}$ *lel*$_3$	1.985(8)	89.0(4)	57.2	(*81*)
$[Co(RR\text{-}ptn)_3]^{3+}$ *ob*$_3$	1.99(3)	87.9(1)	55.9	(*80*)
$[Co(RS\text{-}ptn)_3]^{3+}$ *chair*$_3$	1.99(1)	90(2)	59.7	(*82*)
mer-$[Co(ama)_3]^{3+}$	2.00(2)	85.1(2)	51.1	(*88a*)
$[Co(1,4\text{-}bn)_3]^{3+}$	1.991(6)	90(2)	55.7	(*90*)
mer-$[Co(dien)_2]^{3+}$	1.96(2)	85.1(4)		(*98*)
u-*fac*-$[Co(dien)_2]^{3+}$ ($\lambda\delta,\lambda\delta$)	1.965(6)	85.9(5)		(*100*)
u-*fac*-$[Co(dien)_2]^{3+}$ ($\delta\delta,\delta\delta$)	1.963(9)	85.3(4)		(*100*)
s-*fac*-$[Co(dien)_2]^{3+}$	1.96(1)	86.9(5)	60.0	(*101*)
mer-$[Co(dpt)_2]^{3+}$	2.01(3)	94(3)		(*105*)
fac-$[Co(tap)_3]^{3+}$	1.956(9)	84.9(8)	60.0	(*109*)
$[Co(R\text{-}Metacn)_2]^{3+}$	1.974(5)	85	52.4	(*122*)
$[Co(tach)_2]^{3+}$	1.987(7)	90.0(3)	60.0	(*116*)
$[Co(tame)_2]^{3+}$	1.972(3)	88.9(7)	55.8	(*113*)
f_4-RSRS-$Co(linpen)]^{3+}$	1.977(4)	85.8(9)	56.3	(*126*)
mer-$[Co(18N6)]^{3+}$	1.97(1)	85.2(1)		(*145*)
fac-$[Co(18N6)]^{3+}$	1.997(1)	83.6(1)	60.0	(*146*)
mer-$[Co(21N6)]^{3+}$	1.98(4)	83.6(6)"5-mem" 90(3)"6-mem"		(*145*)
$[Co(taetacn)]^{3+}$	1.991(2)	84.9(1) "en" 87.3"tacn"	48.9	(*127*)
$[Co(taptacn)]^{3+}$	2.008(17)	86.3(3)"tacn" 93.0(3)"6-mem"	59.5	(*129*)

TABLE I (*Continued*)

Complex	Co–N (Å)	Chelate bite angle (degrees)[b]	Trigonal twist, ϕ[c] (degrees)	Reference
$[Co(tae\text{-}en)]^{3+}$	1.98(2)	85.2(1)"arms" 89.5(6)"backbone"		(*132*)
$[Co(tae\text{-}pn)]^{3+}$	2.00(5)	82.5(1.5)"arms" 92(1)"backbone"		(*136*)
$[Co(tae\text{-}tn)]^{3+}$	1.97(4)	85.8(7)"arms" 95.5(7)"6-mem"		(*138*)
$[Co(RR\text{-}tae\text{-}ptn)]^{3+}$	1.98(2)	86.1(4)"arms" 96.2(2)"6-mem"		(*138*)
$[Co(RS\text{-}tae\text{-}ptn)]^{3+}$	1.99(3)	83.9(1.5)"arms" 101(1)"6-mem"		(*138*)
$[Co(sen)]^{3+}$	1.971(5)	86.1	54.5	(*139,140*)
$[Co(stn)]^{3+}$	1.997(9)	94.5	65.3	(*142*)
$[Co(diamcyclam)]^{3+}$	1.941(4)			(*149*)
$[Co(diammecyclam)]^{3+}$	1.957(5)	83.9		(*150*)
$[Co(sep)]^{3+}$	1.990(3)		54.5	(*6,151*)
	1.974(?)	87.0	56.7	(*152*)
$[Co(di(NH_2OH)Sar]^{3+}$ ob_3	1.973(5)	87.4(1)	58.3	(*154*)
$[Co(diNOsar)]^{3+}$	1.982(6)	86.4(1)	54.4	(*153*)
$[Co(captame)]^{3+}$	1.940(13)		50.0	(*155*)
$[Co(NOsartacn)]^{3+}$	1.98(2)	84.3(2)"en" 87.5(2)"tacn"	47.3	(*127*)
$[Co(NH_3)_6]^{2+}$	2.160(5)			(*13*)
	2.183(2)			(*12*)
$[Co(tacn)_2]^{2+}$	2.15(3)	82(1)		(*120*)
$[Co(sep)]^{2+}$	2.164(9)	81.9(3)		(*6*)
$[Co(di\text{-}amHsar]^{2+}$	2.17(2)	81.4(4)	29(1)	(*152*)

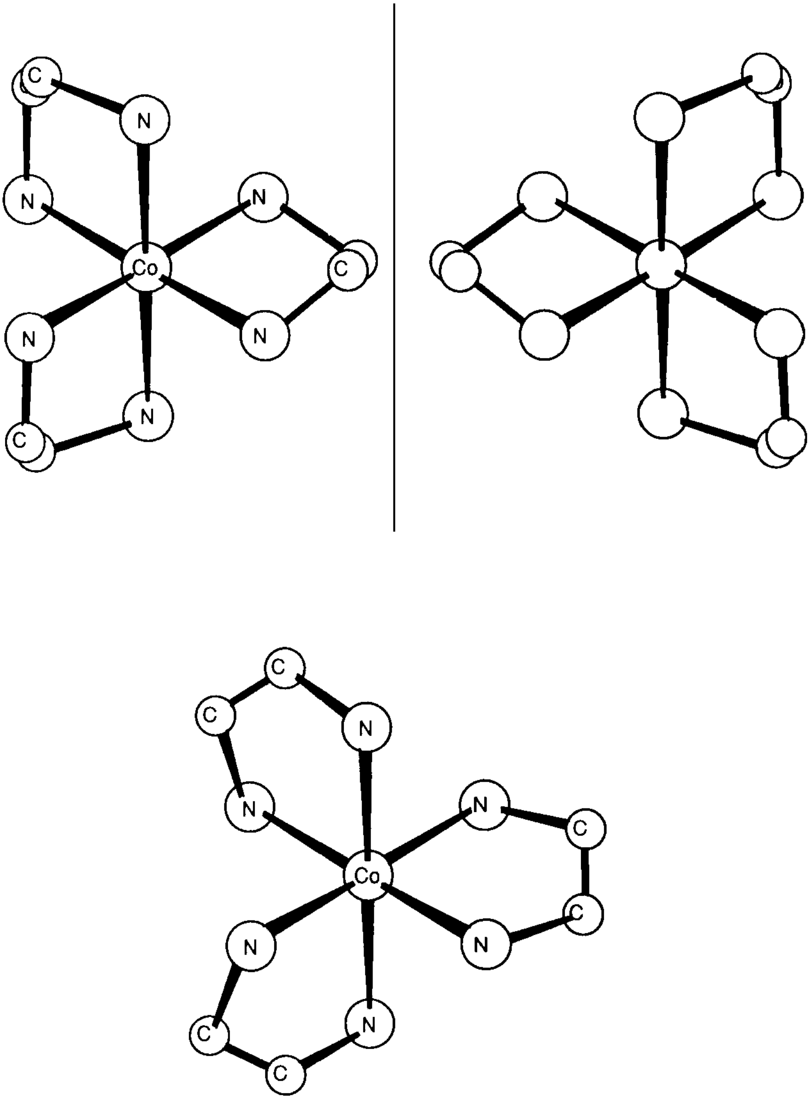
[a] The last four entries are Cobalt(II).

[b] In the column referring to the chelate bite angle the parentheses indentify the particular rings where more than one type of chelate ring exists in the complex; 5-*mem* = 5-membered chelate ring, etc.

[c] The trigonal twist angle ϕ is defined in Fig. 5.

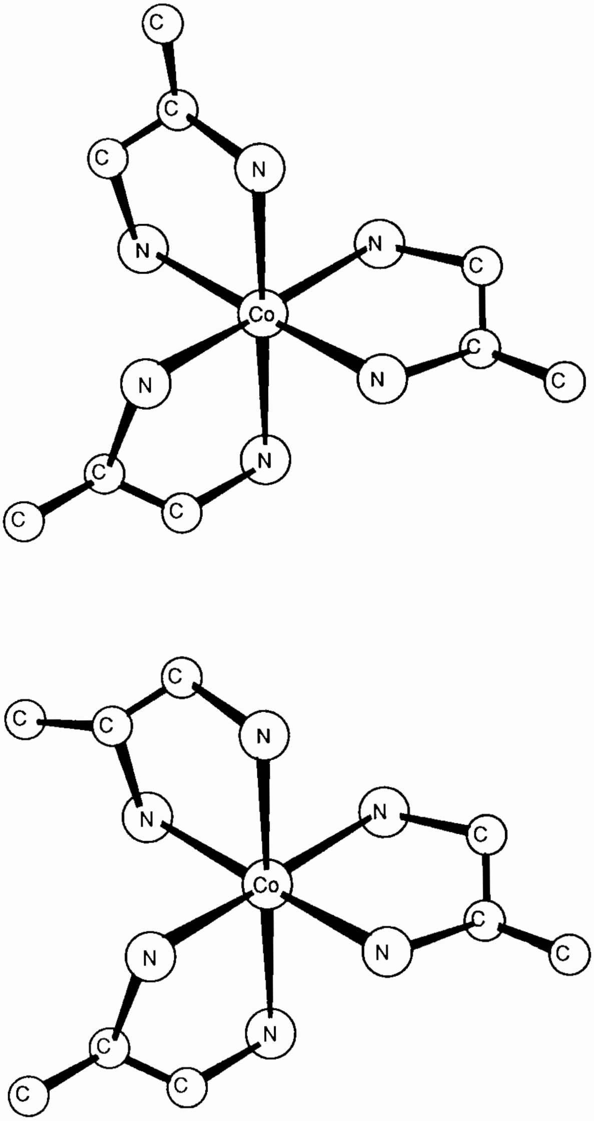
[d] The error shown in parenthesis as the uncertainty in the last quoted figure is the standard deviation of the mean or the published standard deviations of the individual measurements, whichever is greatest.

4.8 kJ mol^{-1} higher than the lel_3 (*17*). Allowing for statistical factors (there are three-possible lel_2ob but only one lel_3 conformer) by adding $-RT \cdot \ln(3/1)$ (-2.7 kJ mol^{-1}) to the ΔH value for lel_2ob gives both conformations the same ΔG value and therefore the same abundance in solution. It has been estimated from NMR data that at 25°C in aqueous solution $[Co(en)_3]^{3+}$ exists as 70% lel_2ob and 30% lel_3, neglecting the



(a)

FIG. 1. (a) Λ *lel*$_3$, mirror image Δ lel$_3$ and Λ *ob*$_3$ [Co(en)$_3$]$^{3+}$, viewed down the threefold axis. (b) Λ *ob*$_3$ [Co(pn)$_3$]$^{3+}$ *fac* and *mer* isomers, viewed down the threefold axis.



(b)

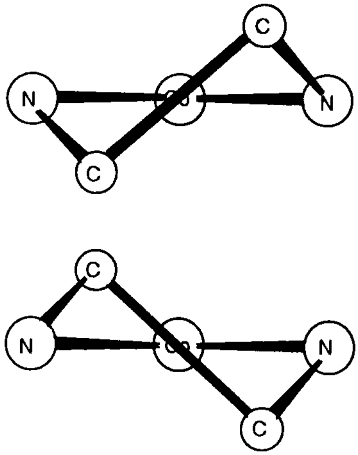


FIG. 2. The λ and δ conformations for five-membered chelate rings.

small amount of the the other conformers (*20*). Recent work using vibrational CD (*22*) to probe the conformations of the rings has estimated that $[Co(en)_3]^{3+}$ in Me_2SO has a 75% *lel* population. This is equivalent to an isomer ratio $lel_2ob : lel_3$ of 3 : 1 if the contribution of the other conformers are neglected. In addition high concentrations of Cl^- ions were shown to favor the *lel* conformation. The proportion of the lel_3 conformer in solution can be increased by addition of phosphate or selenate to the solution (*20, 21*), the lel_3 conformer being the only one that has the correctly oriented N–H bonds to strongly H-bond with these anions. A crystallographic study of the interaction of $HPO_4{}^{2-}$ and $[Co(en)_3]^{3+}$ shows (*23*) the cation in the lel_3 conformation and the phosphate group "capping" the C_3 face with two strong hydrogen bonds to the amine protons (Fig. 3). A similar H-bonded structure is observed for the arsenate salt (*24*). Of course in the solid state the conformers are "frozen out" and lel_3 (*23, 25, 26*), lel_2ob (*27, 28*), and $lelob_2$ (*29, 30, 31*) have been observed in crystallographic studies. For $[Cr(en)_3]^{3+}$ all four conformers have been observed in the solid state (*32–35*). The structure of the $[Co(en)_3]^{3+}$ cation has been determined many times; the lel_3 conformer is the most commonly observed. The lel_3 complex has at least pseudo D_3 symmetry. The structure of the $Co–N_6$ core differs significantly from an octahedron, due to the compression of the bite angle of

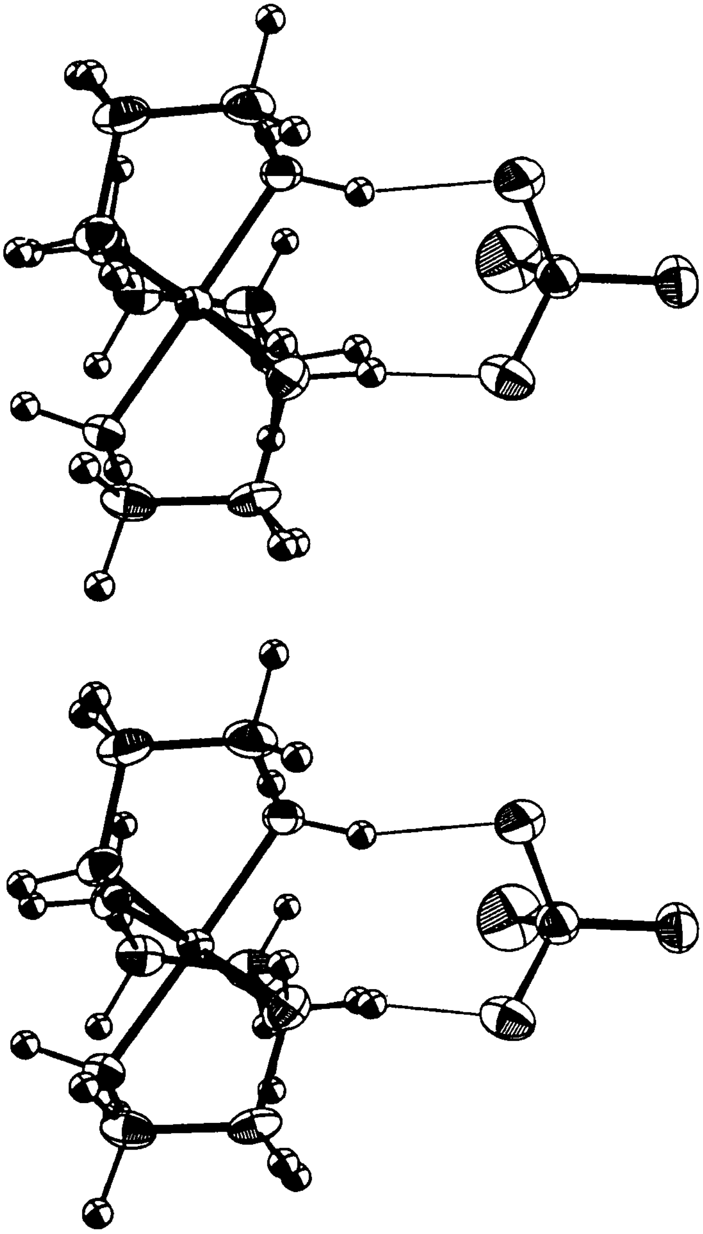


FIG. 3. A stereo pair showing the protonated phosphate ion lying almost on the threefold axis of the $[Co(en)_3]^{3+}$ cation, "capping" that face.

the ligand: 85.5° in the chloride-tartrate salt (*25, 26*). The complex is trigonally twisted only slightly, $\phi = 55°$ (*36*).

b. 1,2-Diaminopropane (pn). $[Co(\pm-pn)_3]^{3+}$ has 48 possible isomers (*37*). In addition to the enantiomeric pairs, Δ and Λ, there are the *lel*, *ob* conformations of the three chelate rings and the stereoisomers, *fac*-ial and *mer*-idional, describing the position of the methyl groups (Fig. 1). Depending on the conformation of the ring and the configuration of the ligand, the methyl group can be oriented either axially or equatorially with respect to the five-membered chelate ring. Complexes that have the methyl group in an axial position are much less stable than complexes with equatorially oriented methyl groups (*15*) and have never been observed. The interplay between these three factors results in 24 observable isomers, many of which have been isolated (*37*). As a result of the strong preference for the equatorial positioning of the methyl groups, *R* and *S* pn coordinate in the λ and δ conformations, respectively. Therefore a complex mixture containing only *R*-pn appears to contain Δ-$\lambda\lambda\lambda$ (lel_3) and Λ-$\lambda\lambda\lambda$ (ob_3) complexes only (*37*); a mixture of *R* and *S* isomers of pn is necessary to form lel_2ob and $lelob_2$ complexes. The geometric (*mer*/*fac*) isomerization has very little effect on either the energy, (*38, 39, 40*) or the absorption and CD spectra (*37*) of the isomers. Even the ^1H NMR of the *mer* and *fac* forms of the ob_3 complex are apparently identical (*41*). Not surprisingly, therefore, the separation of *mer* and *fac* isomers is difficult (*37, 41, 42*) and has only been achieved for the lel_3 (*40*) and ob_3 (*41*) forms. The relative stabilities of the conformers have been studied at 100°C in the presence of Cl^- ions using charcoal as a catalyst (*37*). The relative amounts of isomers is under those conditions lel_3 35%, lel_2ob 41%, $lelob_2$ 18%, and ob_3 4%. The steric interaction of rings in the two conformations is in energy terms, *lel-lel* < lel-ob < ob-ob. X-ray structures of the lel_3 and ob_3 *fac* isomers (*43, 44*) show the complexes with similar bond angles and degree of trigonal twist but significantly different bite angles. In a structure of a mixture of *mer* and *fac* isomers of $\Delta[Co(R\text{-}pn)_3]^{3+}$ (lel_3) the methyl groups are disordered (*45*).

c. *2, 3-Diaminobutane (2, 3-bn).* For the racemic ligand eight isomers of the tris complex are possible while all the methyl groups remain in equatorial positions. Strain energy minimization studies on all the possible isomers and conformers of $[Co(2, 3\text{-}bn_3]^{3+}$, with both meso and racemic ligands, concluded that the presence of an axially oriented methyl group significantly adds to the total strain of the complex (*17, 46*). The lel_3 complex has the lowest strain enthalpy; however, allowing for statistical factors both lel_2ob and $lelob_2$ are calculated to be more abundant than *lel*$_3$, but experimentally *lel*$_3$ accounts for ~60% of the product (*46*). The three lowest energy isomers of the complex of the racemic ligand, *lel*$_3$, *lel*$_2$*ob*, and *lelob*$_2$, have been isolated and characterized by ^{13}C NMR (*46*).

The *meso* 2,3-bn (*RS*-2,3-bn) forces one methyl group to be axial in either skew conformation. In addition the ligand now has distinguishable ends, making facial and meridional isomers possible (*47*). The axial methyl group however destabilizes the ring so that no low-energy conformer exists (*17*). Experimentally, the conformational changes are rapid on the NMR time-scale at room temperature, and therefore individual conformers cannot be isolated (*46*). It was also found that, like $[Co(en)_3]^{3+}$, the proportion of the *lel*$_3$ conformer in solution could be increased by addition of sulfate or phosphate ions (*46*). The chelate ring is predicted to be significantly flattened relative to the rings in $[Co(en)_3]^{3+}$, to relieve the nonbonded interactions between the axial methyl and the neighboring amine protons (*17, 46*).

d. 2-Methyl-1, 2-diaminopropane (ibn). The ligand 2-methyl-1, 2-diaminopropane (ibn) has two methyl groups substituted at one carbon of the ethylenediamine. In either skew conformation, λ or δ, one of the methyls must occupy an axial position. Hald and Rasmussen (*48, 49*) have estimated that the most stable isomer in the $[Co(ibn)_3]^{3+}$ series is the *mer-lel*$_3$, followed by *fac-lel*$_3$ some 0.5 kJ mol^{-1} higher in energy. In this series of complexes the difference in energy between the *ob* and *lel* conformations is predicted to be about 3.9 kJ mol^{-1} for the *fac* series and on average 2.7 kJ mol^{-1} for the *mer* series. In comparison with $[Co(en)_3]^{3+}$, the $[Co(ibn)_3]^{3+}$ chelate rings are predicted to be more flattened, to alleviate some of the strain induced by the axial methyl group.

Kojima et al. (*50*) have synthesized and separated the isomers of $[Co(ibn)_3]^{3+}$. The complexes separated (enantiomeric pairs), *mer* Δ and Λ and *fac* Δ and Λ, all have essentially identical absorption spectra. The absolute configuration of the complexes were assigned on the basis of the signs of the CD transitions in the region of the first *d-d* transition. ^{1}H NMR was used to assign the geometrical isomerism; the *fac* isomers show only two methyl signals, whereas the *mer* isomers display a complex spectrum. The crystal structure of the Δ *fac* isomer was claimed to confirm the assignment (*50*); however, the complex ion was disordered and the structure refinement was not completed (*51*). The structure determination of the *mer* complex has recently been completed (*52*): The chelate bite angle is 84.3(9)°.

The next ligand in this series of increasingly substituted ethylendiamines would be the 2-methyl-2,3-diaminobutane; however, it appears that complexes of this ligand have not been studied.

e. 2,3-dimethyl-2,3-diaminobutane (tmen). This ligand, like en, has no stereogenic center, and only eight isomers are possible via the usual Δ, Λ, *lel*, *ob* interplay. A strain energy minimization of the conformers of $[Co(tmen)_3]^{3+}$ has revealed a regular increase in the total strain energy of the complex with increasing *ob* content of about 4 kJ mol^{-1} per *ob* ring (*53*). The structure of the racemic complex as the tosylate salt (*53*), however, has the ob_3 conformation, as has the sulfate salt (*54*). The observation of the ob_3 conformation for two salts, both of which may have been expected to stabiize the lel_3 structure, casts some doubt on the veracity of the molecular mechanics calculations. The presence of six axially disposed methyl groups makes the complex highly strained and unusually reactive: The mean Co–N bond length is 1.999(6) Å; the trigonal twist, ϕ, is the largest observed for a tris chelate amine complex of this type, 44°; and the chelate bite angle is only 80° (*53*).

f. 2,3-Diaminopropanol (dap). $[Co(dap)_3]^{3+}$ was prepared using unresolved ligand. No stereochemical or structural questions were addressed. The spectrum of the complex indicated the $Co-N_6$ core despite the presence of potentially chelating alcohol groups (*55*).

g. 3,3-dimethyl-1,2-diaminobutane (dmbn). Dmbn is similar to pn except that the methyl group of pn is replaced by a *t*-butyl group in dmbn. One might expect intuitively the complexes of dmbn to behave like pn except that its conformational preferences would be more extreme. This is essentially what is observed. *S*-dmbn coordinates in the δ comformation. Two studies on the $[Co(S\text{-dmbn})_3]^{3+}$ complexes have been reported. In the first of these, Kojima and Fujita (*56*) reported that only the *mer* and *fac* Λ isomers were produced. Under equilibrium conditions (i.e., 100°C in the presence of active charcoal for several hours), the isomers were produced in equal amounts, with no formation of any Δ (i.e., ob_3) isomers. The absolute configurations of the complexes were assigned by comparison of the CD spectra to those of $[Co(pn)_3]^{3+}$ complexes and the geometrical isomers on the basis of ^1H NMR, which showed one methyl peak for the *fac* isomer and two for the *mer* isomer. Therefore the *lel*/*ob* preferences for this ligand are significantly stronger than for pn, so much so that no complexes with the *ob* conformation are observed at all.

The second report on the preparation of this series of complexes came about six months later, from Hawkins and Martin (*57*). In contrast to the previous result, only one isomer of the $[Co(S\text{-dmbn})_3]^{3+}$ series was observed. ^1H and ^{13}C NMR of this product indicated that it was the *fac* isomer; only one methyl resonance was observed and one signal for each type of carbon in the dmbn ligand. The CD of the complex was also similar to that previously observed for the *fac* isomer. The explanation for this conflict may lie in the different methods used to isolate the complexes.

h. 1,2-cyclopentanediamine (cptn). Racemic 1,2-diaminocyclopentane (cptn) forms strained bidentate complexes. The conformation of the ring is absolutely fixed as δ for *SS*-cptn and λ for *RR*-cptn. In the most recent report (*58*) on the synthesis of the $[Co(\pm{-}cptn)_3]^{3+}$ complexes no ob_3 complex was detected. The lel_3, lel_2ob, and $lelob_2$ complexes were formed in the ratio 10 : 4 : 1, indicating a fairly strong preference for *lel* rings, much more so, for example, than observed for $[Co(\pm\text{-chxn})_3]^{3+}$ (*vide infra*). An earlier study (*59*) using only *SS*-cptn reported that the Δ-lel_3 and Λ-ob_3 form in an approximately 10 : 1 ratio. The later study (*58*), however, casts much doubt on this observation and suggests that the complex assigned at the Λ-ob_3 may in fact be the Δ-lel_2ob isomer produced as a result of an incomplete resolution of the ligand. The absorption and CD spectra reported for the Λ-ob_3 (*59*) isomer are consistent with those reported for Δ-$[Co(SS\text{-cptn})_2(RR\text{-cptn})]^{3+}$. A crystal structure (*60*) of the $(-)_{589}[Co(+\text{-cptn})_3]Cl_3 \cdot 4H_2O$ found, as expected, that the complex is the Λ-$[Co(SS\text{-cptn})_3]^{3+}$ cation and the rings are all in the *lel* conformation. Although the structure determination suffers from rather large standard deviations, it is possible to see that the strain manifests itself in elongated Co–N bond lengths (2.00(2) Å). The strain inherent in the complex ion is also apparent from the substitution lability of the complex.

The *meso*-cptn (*RS*-cptn) ligand chelates much more readily than (±)-cptn; the tris complexes of *meso*-cptn also generate the stereoisomers *mer* and *fac*. The complexes of $[Co(RS\text{-cptn})_3]^{3+}$ have been separated into Δ and Λ forms (*59*). Very little is known about the conformation of the rings in these complexes. The reduced strain in comparison to the complexes of the racemic ligand is apparent from the relative lability of the two complexes.

i. 1,2-Diaminocyclohexane (chxn). The $[Co(\pm\text{-chxn})_3]^{3+}$ system displays the familiar interplay between configuration and conformational isomerism. The (*R*)-chxn coordinates in the λ conformation and vice versa for (*S*)-chxn. Eight isomers are possible (with all ring substituents equatorial) in the $[Co(\pm\text{-chxn})_3]^{3+}$ system. At 100°C in the presence of charcoal lel_3, lel_2ob, $lelob_2$, and ob_3 are present in the relative amounts 47 : 35 : 14 : 3.2. All these isomers have been separated and characterized (*61*). The steric energy of chelate ring interactions is *lel-lel* < *lel-ob* < *ob-ob*; that is, the strain energy contributed to the system by a particular ring conformation is dependent on the conformation of the neighboring rings.

To our knowledge no tris complexes of the *cis* or *meso* chxn ligand have been prepared.

j. 1-Aminomethyl-2-methylcyclyohexylamine (meamcha). 1*R*,2*S*-1-aminomethyl-2-methylcyclyohexylamine (*RS*-meamcha) is a C_1 disubstituted ethylenediamine and therefore must have one axial and one equatorial substituent in either skew ring conformation. Saito and Kidani (*62*) separated the isomers of $[Co(RS\text{-meamcha})_3]^{3+}$. Only the λ conformation of the ligand was observed and the lel_3 conformation was roughly three times as abundant as the ob_3 for both the *mer* and *fac* isomers. The ligand therefore coordinates preferentially with the C_1–C_2 bond of the cyclohexane ring oriented equatorially. Presumably the alternate conformation results in the 2-methyl group contacting the neighboring amine group. The tris 1-aminomethylcyclohexylamine complexes of Co(III) have been reported, but little is known about their structure (*63*).

k. 1-Phenyl-1,2-diaminoethane (pen). Pen is typical of other C-substituted en rings and the phenyl substituent is preferentially equatorially oriented; therefore the *R*-pen forms rings of λ comformation. Kojima and Fujita (*56*) have separated the four possible isomers of $[Co(R\text{-pen})_3]^{3+}$: *mer*, *fac*, Δ, and Λ. The *lel*:*ob* ratio is 5:1, indicating that the *ob* conformation was not as strained as for dmbn where no *ob* isomers are observed, or the complexes of $[Co(pn)_3]^{3+}$ where a lel_3/ob_3 ratio of ~9:1 is observed (*37*).

l. 1,2-Diphenyl-1,2-diaminoethane (dpen). Two isomers of $[Co(SS\text{-dpen})_3]^{3+}$ have been prepared, and $(-)[Co((SS-)\text{dpen})_3]^{3+}$ predominates over the $(+)[Co((SS-)\text{dpen})_3]^{3+}$ complex at equilibrium (*64*). An X-ray structure of the $(+)[Co((SS-)\text{dpen})_3](NO_3)_3 \cdot H_2O$ complex (*65*) (the minor component at equilibrium) found it to be the Λ isomer, with all the rings in the *lel* conformation. The two phenyl rings apparently stabilize the ob_3 conformation of the complex.

m. N-methyl-1,2-diaminoethane (meen). The tris complexes of this ligand have been known for some time (*66*); however, a thorough report has appeared recently (*66a*). There are twelve possible stereoisomers of $[Co(meen)_3]^{3+}$. Only three racemic stereoisomers of the complex were observed in this study, and all were judged to have the same gross structure (i.e., *mer* or *fac*) because of the facility of interchange between the three isomers. The isomers are therefore *N*-H diastereomers with the same arrangement of the *N*-CH_3 groups. THe complexes are thought to be the *mer* complexes because all appeared to have lower than C_3 symmetry, which at least some of the *fac* isomers should display in the the ^{13}C NMR. Several other *N*-alkylated en_3 derivatives have been prepared (*67*).

2. *Six-membered Rings*

Six-membered chelate rings commonly adopt the chair or symmetrical-skew boat conformations in Co(III) complexes (Fig. 4). More distorted conformations are also possible; for example, the unsymmetrical-skew boat (*68*). The symmetric boat conformation has never been observed and is predicted to be extremely strained. The

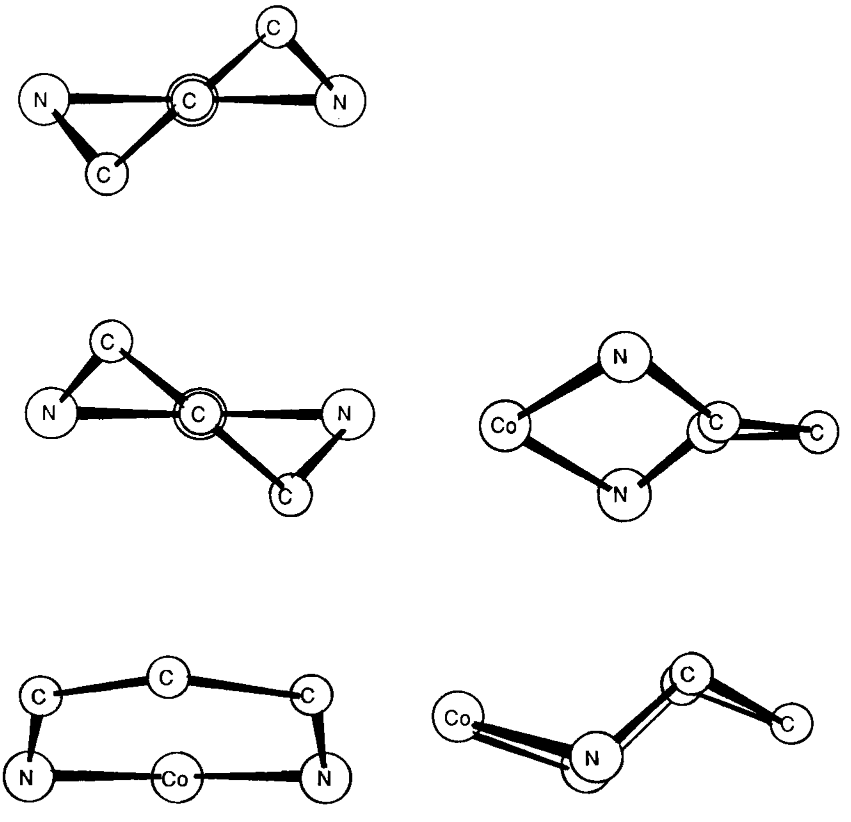


FIG. 4. Symmetric conformations observed for six-membered chelate rings, λ-skew boat, δ-skew boat, and chair. Unsymmetric conformations are also observed [see reference (*68*)].

problem of the structure of complexes containing six-membered rings has been approached using X-ray crystallography, molecular mechanics, electronic and NMR spectroscopy.

a. 1, 3-Diaminopropane (tn). X-ray crystallographic studies of $[Co(tn)_3]^{3+}$ as the chloride and bromide salts (*69, 70*) have been carried out. In both cases the rings were in the tris-chair conformation. In the case of the chloride salt (*70*), the carbon atoms, especially the central one, had high thermal anisoptropy in a direction compatible with a symmetrical bending of the chair. Several authors have estimated the relative energies of the various ring conformations for $[Co(tn)_3]^{3+}$. Gollogly and Hawkins predicted that the tris-chair would be slightly more stable than the *lel*$_3$ skew boat conformation (*71*). Rasmussen et al. (*72*) reached a similar conclusion, arriving at 16 unique energy minima corresponding to a variety of defined conformations. Excluding the symmetric boat forms, the highest energies were displayed by the skew boat conformers, *ob*$_2$*lel* and *ob*$_3$. The symmetric boat conformer was not considered, since even in simple models it is apparent that the nonbonded interaction between the central carbon and the amine protons on an adjacent ring would be prohibitive. The structure of the ligands in the tris-chair complex as predicted by Rasmussen compares favorably with those found in the crystal (*69, 70*). The Co–N bond lengths, however are calculated to be on average 0.07 Å longer than observed.

In another study Geue and Snow (*73*) predicted that the *lel*$_3$ skew isomer was lower in energy than that of the tris-chair structure by 0.77 kJ mol^{-1}. This apparent conflict has been ascribed to the fact that Geue and Snow did not include H . . . H interactions of greater than 2.78 Å (*72*).

An examination of the temperature-dependent CD spectra of (+) $[Co(tn)_3]^{3+}$ and the solid state CD of (+) $[Co(tn)_3]Br_3$, the structure of which is known, has led to the conclusion that in solution the tris-chair is the most stable conformer by about 0.5 kJ mol^{-1} over the *lel*$_3$ skew boat (*74*).

The structure of $[Co(tn)_3]^{3+}$ (*70*) is closer to a regular octahedral array of donor atoms than is $[Co(en)_3]^{3+}$. The chelate bite angles average 91°. The mean Co–N bond length is longer than for $[Co(en)_3]^{3+}$.

b. 1,3-diaminobutane (1,3-bn). The most stable conformers of 1,3-bn complexes, like the five-membered rings discussed previously, have the methyl group in an equatorial position with respect to the six-membered ring. Thus (*S*)-1,3-bn forms skew boat rings with the δ conformation and vice versa for (*R*)-1,3-bn. Of course both these ligands can adopt chair conformations. Kojima and Fujita (*75*) have isolated and studied the four diastereomers of $[Co(S\text{-}1,3\text{-}bn)_3]^{3+}$, *mer* Δ, *mer* Λ, *fac* Δ, and *fac* Λ. The similarity of the position of the first *d-d* transition for all the complexes, 489–491 nm, to that of $[Co(tn)_3]^{3+}$ and $[Co(RS\text{-}ptn)_3]^{3+}$ (490 and 491 nm) led them to the conclusion that all the complexes are predominantly in the chair form in aqueous solution. In addition it was concluded that the *fac* Λ conformer was rather more conformationally flexible than the other conformers and was in equilibrium with the δ-skew boat (*lel*) conformer. Sulfate ions induced changes in the CD and absorption spectra of all the isomers. The changes in the Λ forms were interpreted as a shift in the equilibrium toward the Λ δδδ (lel_3) form of the skew boat conformation.

c. 2,4-diaminopentane (ptn). In contrast to the paucity of information on the conformation of 1,3-bn rings, the complexes of ptn have been extensively studied. Three crystal structures, several molecular mechanics studies, and NMR studies have been carried out on the isomers of $[Co(ptn)_3]^{3+}$.

The optically active ligands, *RR*-ptn and *SS*-ptn, adopt skew boat conformations in which both methyls are equatorial (*76*). Thus *RR*-ptn adopts the λ conformation, and *SS*-ptn forms the δ conformation of the skew boat. The *meso* form of the ligand, *RS*-ptn, however, must adopt a chair conformation if both methyls are to be equatorially oriented. Tris complexes composed solely of *RR*- (or *SS*-) ptn are therefore restricted to the lel_3 and ob_3 isomers. Molecular mechanics calculations have predicted that the lel_3 conformation of complexes with the racemic ligands (e.g., Δ λλλ) is significantly (4–7 kJ mol^{-1}) more stable than the ob_3 (Λ λλλ) (*77, 78*). The tris chair form of *RS*-ptn was estimated to be very similar in strain energy to the *RR*-ptn lel_3 complex (*78*).

The $[Co(RR\text{-}2,4\text{-}ptn)_3]^{3+}$ complexes have been synthesized and separated into $(+)_{546}$ and $(-)_{546}$ isomers (*79*). On the basis of their absorption and CD spectra, the $(-)_{546}$ and the $(+)_{546}$ complexes were tentatively assigned as Δ λλλ (lel_3) and Λ λλλ (ob_3), respectively. The lel_3 isomer was produced in about 10-fold excess over the ob_3 isomer. Since the conformation of the *RR*-ptn ligand in the skew boat form is fixed as λ, then once the configuration is known, the conformation of the rings is also known (i.e., *lel* or *ob*). X-ray crystallographic studies on both isomers confirmed the assignments (*80, 81*). In solution, the Λ and Δ forms of $[Co(RR\text{-}ptn)_3]^{3+}$ give intra-ring ^1H coupling constants consistent with exclusive population of the twist boat conformation (*76*).

Also the crystal structure of *fac*-$[Co(RS\text{-}ptn)_3]^{3+}$ (*82*) showed, as predicted from molecular mechanics studies, the tris-chair form with all methyls equatorial. The structural parameters for the six-membered ring framework are rather similar to those for $[Co(tn)_3]^{3+}$.

d. 1-Phenyl-1,3-diaminopropane (phtn). Three of the possible four isomers of (*S*)-1-phenyl-1,3-diaminopropoane (*S*-phtn) have been synthesized, *mer* Δ, *fac* Δ, and *fac* Λ (*83*). The *fac-mer* isomerization is easily distinguished using ^{13}C NMR: *fac* isomers possess C_3 symmetry and *mer* has only C_1. The configuration of the complexes was assigned by comparison of the CD spectra with complexes of known configuration. The preference for equatorially oriented substituents requires that *S*-phtn forms rings in the λ skew boat or chair conformation. Kojima and Fujita (*83*) have assigned the conformation of the chelate rings of $[Co(S\text{-}phtn)_3]^{3+}$ on the basis of the UV/vis absorption and CD spectra. On the assumption that the *lel* skew boat rings give a stronger ligand field than the chair form (*vide infra*), the *fac* Δ isomer is predicted to be, in aqueous solution, predominantly in the *lel* skew boat conformation. In contrast, the *fac* Λ complex, which can form chair or *ob* skew boat rings, is predominantly in the chair conformation. The *mer* Δ isomer has its first *d-d* transition maximum intermediate between that of *fac* Δ and *fac* Λ isomers. This is interpreted as evidence for a significant population of the [chair*lel*$_2$] and [chair$_2$*lel*] conformers.

e. 1,3-diphenyl-1,3-diaminopropane (dppn). Dppn is the diphenyl analogue of ptn. Thus *SS*-dppn (note apparent inversion due to substituent priority rules), forms skew boat rings with the λ conformation, the chair forms being energetically unfavorable due to the requirement for an axial phenyl group in that conformation. Two $[Co(SS\text{-}dppn)_3]^{3+}$ isomers have been synthesized and their properties discussed in terms of the probable ring conformations (*84*). The absolute configuration of the complexes were assigned by their similarity to the CD spectra of the complexes of ptn.

f. 2-Aminomethylcyclohexylamine (chxtn). The complexes of chxtn have two fused six-membered rings per ligand. Noji et al. (*85*) have synthesized tris 1*R*, 2*R* and 1*R*, 2*S* complexes of this ligand. The 1*R*, 2*R*-chxtn yields only *mer* and *fac* Δ complexes. Interestingly the authors did not comment on the absence of the Λ complexes, although there seems to be no *a priori* reason why these isomers should be totally absent. This system is rather complex and assumptions about the relative energies of conformers cannot be made easily. In the λ skew boat form, however, both ring fusions are equatorially disposed. This will probably be the most stable conformer. The tris skew boat conformation Δ λλλ (*lel*$_3$) may be significantly more stable than the *ob*$_3$ conformation (Λ λλλ), therefore explaining the absence of any Λ isomers.

For the 1*R*,2*S*-chxtn complexes (*85*) one chair conformer puts both ring fusions equatorial with respect to the tn ring. In the strict λ skew boat conformation the substituent at the 2 position of the tn ring would be in an axial position. However, the considerable flexibility at that point in the ring allows flattening of the tn ring, generating an unsymmetrical skew boat conformation with pseudo diequatorial ring fusion. It is claimed that the three observed isomers of $[Co(1R,2S\text{-chxtn})_3]^{3+}$ (*85*), *mer*-Λ, *fac*-Λ, and *mer*-Δ, are composed predominantly of rings in these two possible conformations.

g. 2-Methyl-1,3-diaminopropane (metn). Metn forms two tris complexes, *mer* and *fac*, because the methyl group can be oriented toward either side of the chelate ring. Mather and Tapscott (*86*) have separated the $[Co(metn)_3]^{3+}$ complex into the two isomers. The six-membered rings in this complex can adopt several symmetric conformations: chair with axial methyl, chair with equatorial methyl, λ skew boat, and δ skew boat. Little is known about the relative stabilities of the four conformers, although it is probably safe to assume that the chair with the axial methyl will be highest in energy even though the ring substituent is farther removed from steric interactions than in the complexes discussed previously. A partially resolved crystal structure of the *fac*-$[Co(metn)_3]Cl_3$ complex is claimed to show the rings in a skew conformation, although the structure was severely disordered and the refinement abandoned (*86*). The solution ^{13}C NMR and visible spectroscopy were consistent with a predominantly skew boat conformation of the rings.

Further examples of tris complexes with tn rings substituted at the 2 position include 2-hydroxy-1,3-diaminopropane (*87*), 2-bromo-1,3-diaminopropane (*87*), and 2,2-dimethyl-1,3-diaminopropane. (*88*)

h. 3-(Aminomethyl)-3-methylazetidine (ama). The tris complex of this ligand has been synthesized (*88a*). The strain inherent in the tris complex is apparent from the elongated Co–N bond lengths (mean 2.00 Å), the lower energies of the electronic transitions (resulting in the complex having a reddish color), and the propensity of the complex to undergo base hydrolysis. The ligand should be capable of forming both *mer* and *fac* isomers; however, only the *mer* isomer was observed.

3. *Seven-membered Rings*

1,4-Diaminobutane (1,4-bn). Only one example of a cobalt(III) tris complex with seven-membered rings is known. It is the tris(1,4-diaminobutane)cobalt(III) complex, $[Co(1,4\text{-bn})_3]^{3+}$. The complex was resolved by Kojima et al. (*89*). The structure of the $(+)_{589}[Co(1,4\text{-bn})_3]^{3+}$ determined by X-ray crystallographic methods is the Δ λλλ isomer (i.e., the *lel*$_3$) conformation (*90*). To our knowledge no molecular mechanics or other studies have been conducted on the relative stabilities of the conformers of any seven-membered chelate rings. The X-ray structure shows considerable strain in the rings. The complex has a more nearly octahedral array of N donors than $[Co(en)_3]^{3+}$ (*90*) (see Fig. 5).

C. TRIDENTATE LIGANDS

1. *Linear Amines*

a. 1,5-Diamino-3-azapentane (dien). The bis complexes of dien form three geometric isomers: *mer*, unsymmetric facial, and symmetric facial (u-*fac* and s-*fac*). The u-*fac* and s-*fac* isomers have the secondary amines *cis* and *trans* to each other, respectively (Fig. 6). A very thorough study of the equilibrium distribution of the isomers of $[Co(dien)_2]^{3+}$ has been made by Keene, Searle, and co-workers (*91, 92, 93*) and by Yoshikawa and Yamasaki (*94*). In aqueous solution at 18°C with Cl^-, Br^-, NO_3^-, and ClO_4^- counter ions the isomer distribution was independent of anion with a *mer*, u-*fac*, s-*fac* ratio of ~64 : 29 : 7 (*93*). Higher temperature increased the proportion of *fac* isomers. The presence of the oxo ions of trigonal symmetry, PO_4^{3-}, SO_4^{2-}, and SeO_3^{2-}, increased the yield of the s-*fac* isomer, up to 59% of the total in the case of 0.4 M PO_4^{3-}. This has been interpreted as evidence for the formation of relatively strong H-bonded ion pairs between the anions and the s-*fac* isomer. The other isomers do not possess the required geometry to strongly H-bond with these anions. The measured ion

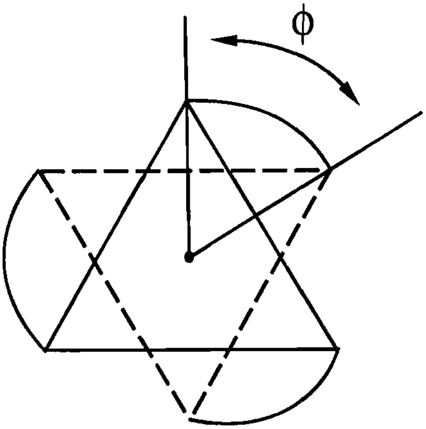


FIG. 5. The trigonal twist angle ϕ for a tris-bidentate complex.

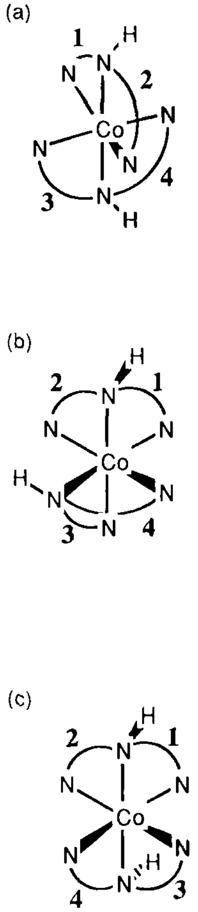


FIG. 6. The geometrical isomers of $[Co(dien)_2]^{3+}$: (a) (δ-NH)-*mer*, (b) (Λ)-u-*fac*, and (c) s-*fac*.

pairing constants for PO_4^{3-} decrease in order s-*fac* (5500 M^{-1}), u-*fac* (850 M^{-1}), *mer* (84 M^{-1}) (*93*). The s-*fac* isomer has a center and plane of symmetry and therefore has no optical isomers; the u-*fac* isomer has only a 2-fold rotation axis and exists as a pair of enantiomers. The *mer* isomer exists as a pair of enantiomers also; however, the dissymmetry in the molecules exists solely as a result of the stereochemical relationship between the puckered chelate rings on each ligand. This is different from the "normal" conformational and vicinal effects, since one-half of each dien ring adopts a conformation that is the mirror image of the other; thus these effects are internally compensated. The asymmetry can be defined by the relationship between the N–H bonds of the two secondary amines. These bonds define a skew pair of lines, thus giving rise to the designation of the isomers as *mer*-δ-NH and *mer-λ-NH (91, 92)*. The successful resolution of *mer* enantiomers is dependent in the inertness of the secondary amine and can be achieved only in acidic solution. All the possible optical and geometric isomers of $[Co(dien)_2]^{3+}$ have been separated (*91, 94*) and their physical properties recorded.

The $[Co(dien)_2]^{3+}$ system has been the subject of several molecular mechanics studies. Two early studies (*95, 96*) did not reproduce the observed isomer ratio. The most recent, however, by Bond et al. (*97*), was more successful. Each of the four five-membered chelate rings in $[Co(dien)_2]^{3+}$ can, in principle, adopt either the δ or λ conformation, giving rise to a large number of conformers; however, some combinations are not sterically feasible. Bond et al. considered all the possible conformers of the three geometric isomers in both the Co(II) and Co(III) oxidation states. The minimum energy conformation of the *mer* isomer, of the eight possible, is (δλ,δλ); (the conformation of each chelate ring in the order shown in Fig 6). This is also the structure observed in the solid state (*98, 99*), and there is generally good agreement between the predicted and observed structural parameters for the bromide salt (*98*). The nitrate salt (*99*), however, deviates significantly in the angles around the carbon atoms from both the bromide salt and the structure predicted by molecular mechanics. The geometry around the metal center of the two structures are quite similar however, and both show considerable shortening of the central secondary amine Co–N bonds 1.940(8) (*98*), 1.947(8) Å (*99*) All other *mer* conformers are predicted to be much higher in energy than the (δλ,δλ) and are not expected to contribute to the solution properties of *mer*-$[Co(dien)_2]^{3+}$.

Eight conformations are possible for the u-*fac* isomer; of these the (λδ,λδ) conformer (Fig. 6) is predicted to have the lowest strain energy, although several conformations should be populated in solution. Consistent with this, enantiomers of both the (λδ,λδ) and the (δδ,δδ) conformers are observed in the crystal structure of the hexcyanocobaltate salt (*100*). Both the predicted structures are in reasonable agreement with the observed solid state structures. The Co–N bond lengths for the u-*fac* complexes do not show the same variation as the *mer* complex. The secondary amine has a fairly typical Co–N bond length (for the two conformers) 1.970(4) (λδ,λδ) and 1.968(4) Å (δδ,δδ).

The higher symmetry of the s-*fac* isomer means that only seven distinct conformers are possible. In the Co(III) complex, the (λδ,λδ) isomer is the lowest in strain energy, the next lowest being ~7 kJ mol^{-1} higher, so (λδ,λδ) should predominate in solution. The crystal structure of s-*fac*-$[Co(dien)_2]Br_3$ (*101*) has the predicted conformation, and the structure is reproduced well by molecular mechanics. The secondary amine has a slighty shorter Co–N bond length than the primary amines in this case, although the difference is barely significant. The chelate bite angles are significantly larger than in either of the previous isomers.

The study by Bond et al. (*97*), although correctly predicting the sequence of free energy differences for the geometrical isomers (*mer*, u-*fac*, s-*fac*), tended to over estimate the energy differences so that the predicted abundances of the two *fac* isomers were less than observed.

b. 1,6-Diamino-3-azahexane (pet). To our knowledge the $[Co(pet)_2]^{3+}$ complex has only been synthesized by Ventur et al. (*102*). In that study the geometry of the complex was not specified and it may have been a mixture of *mer* and *fac* isomers, or it may form only the *mer* isomer like $[Co(dpt)_2]^{3+}$ (*vide infra*).

c. 1,7-Diamino-4-azaheptane (dpt). $[Co(dpt)_2]^{3+}$, first reported by Schlessinger (*103*), has been studied in detail by Searle and Hambley (*104, 105*). The complex can only be formed in nonaqueous solvents, and only the *mer* isomer is produced. The complex is very prone to hydrolytic loss of one dpt ligand in neutral and basic solution, a fact which precludes isomerization studies. The ^{13}C and ^{1}H NMR spectra of the complex are consistent with a rapid equilibrium between the various ring conformations.

A molecular mechanics study of the system (*105*) has found that the $(chair)_4$ conformer of the *mer* isomer has the lowest overall energy, although several others were predicted to be significantly populated in solution. The *mer* isomers were significantly more stable (by 20 kJ mol^{-1}) than either of the *fac* isomers, in keeping with their nonobservation. A crystal structure of *mer*-$[Co(dpt)_2]^{3+}$ (*105*) found the $(chair)_4$ conformation as predicted. The observed structure was reproduced fairly well by the calculations. The ^{13}C NMR shows only time-averaged signals for the two carbons closest to the primary amine, in agreement with the prediction that several conformations are populated in solution (*104*). The carbons bonded to the secondary amine are more conformationally restrained, and two ^{13}C NMR signals were observed.

d. 3-Methyl-1,5-diamino-3-azapentane (medien). The bis medien complexes of Co(III) were originally synthesized primarily out of interest in the unusual asymmetry expected for the *mer* isomer, analogous to that observed for *mer*-$[Co(dien)_2]^{3+}$ (*106, 107*). However, only the s-*fac* isomer of $[Co(medien)_2]^{3+}$ has been synthesized. Neither of the other isomers have ever been observed, despite one erroneous reference to u-*fac*-$[Co(medien)_2]^{3+}$ (*108*). Kojima et al. (*107*) conducted a molecular mechanics study of the isomers of $[Co(medien)_2]^{3+}$ considering, however, only those conformers found in the crystal structures of $[Co(dien)_2]^{3+}$. Despite this limitation, the s-*fac* isomer was predicted to be by far the most stable of the three isomers, 10 kJ mol^{-1} more stable than the *mer* and 21 kJ mol^{-1} more than the u-*fac*.

2. *Branched Amines*

a. 1,2,3-Triaminopropane (tap). Tap is capable of coordinating only in a *fac* manner. One report (*109*) of the preparation of the $[Co(tap)_2]^{3+}$ complexes gave the impression that only the s-*fac* isomer was produced. The X-ray structure (*109*) of the chloride salt of the complex shows the two terminal amines at fairly typical distances from the central metal ion, whereas the Co–N bond length to the central amine is significantly shortened (1.942(2) Å). ^{13}C NMR of the complex showed only two types of carbon atom consistent with the s-*fac* isomer. In that report the possibility of another isomer was not discussed. A more recent report (*110*) of the preparation of this complex has considered both isomers and separated them in an approximately 45 : 55 ratio, the u-*fac* being the most abundant, in good agreement with estimates using molecular mechanics. The ^{13}C NMR spectra were recorded for the separated isomers and shown to be measurably different, the u-*fac* isomer spectrum consisting of three signals. The s-*fac* isomer is the least soluble of the two as the chloride salt; this may be the reason that the u-*fac* isomer was overlooked in the previous study. Molecular models show that the rings are conformationally rigid, being fixed in a (distorted) δ, λ pair for each ligand as found in the solid state.

b. 2-Methyl-1,2,3-triaminopropane (tamp). Tamp forms u-*fac* and s-*fac* isomers analogous to the bis complexes of tap. The two isomers have been separated (*111*); the complexes can be distinguished by their ^{13}C NMR: the u-*fac* shows four signals, the s-*fac* only three. The u-*fac* and s-*fac* complexes are formed in a 35 : 65 ratio, in contrast to the statistically expected 67 : 33.

c. 1,2,4-triaminobutane (tab). The bis complex of tab has been prepared by two groups of workers (*102, 112*). This ligand is constrained to the *fac* mode of coordination but has a degree of flexibility possible in the conformation of the six-membered ring that can adopt either a skew boat or chair form (*112*). In addition to the geometric isomers, the ligand is asymmetric, which results in a total of five distinct isomers. Complexes of the resolved ligand are restricted to only three isomers; the racemic ligand is necessary to produce all five isomers. The isomers have been separated by HPLC and ^{13}C NMR data collected for all complexes; the relative yields of the three isomers were in agreement with their distribution predicted by molecular mechanics (*112*).

d. 1,1,1-Tris(aminomethyl)ethane (tame). Tame, like the previous two ligands, is constrained to coordinate facially. Depending on the relative conformations of the two ligands the $[Co(tame)_2]^{3+}$ complex will have either D_3 or C_{3i} symmetry. If the conformations of the two ligands are the same then the complex will be asymmetric, and the $\delta\delta$ and the $\lambda\lambda$ conformers (D_3) are enantiomeric. The $\delta\lambda$ (*meso*) conformer is centrosymmetric. A molecular mechanics study of the two isomers of $[Co(tame)_2]^{3+}$ predicted that the racemic form was 6.7 kJ mol^{-1} more stable than the *meso* form (*113*). The inversion of conformation of one of the ligands, although requiring no bond breaking, occurs by a trigonal twist of the entire ligand [the three fused six-membered rings pass through an eclipsed (tris-boat) symmetrical transition state]. The complex can be resolved in the solid state by crystallization as the chloride--tartrate salt, but rapidly isomerizes in solution. The X-ray structure of $(+)_{589}$-$[Co(tame)_2]Cl(tartrate)$ shows the conformation of the chelate rings in the λ-unsymmetrical skew boat form, thus giving the complex overall chirality Δ (*113*). The complex is slightly trigonally twisted ($\phi = 55.8°$); the twist apparently relieves some proton-proton nonbonded interaction between the ligands.

e. 1,3,5-triaminocyclohexane (tach). Reaction of $Na_3[Co(CO_3)_3]$ with a mixture of the tach isomers (i.e., 1(e),3(e),5(e)-tach and 1(e),3(e),5(a)-tach] (*114*) yields only $[Co(1(a),3(a),5(a)\text{-tach})_2]^{3+}$ (*115*) (hereafter referred to as $[Co(tach)_2]^{3+}$. Only one isomer and conformer are possible for this complex. An X-ray study shows the complex with the expected structure, that is, *fac* geometry with all rings in the chair conformation (*116*).

f. 1-methyl-2,4,6-triaminocyclohexane (metach). 1(e)-methyl-2(e), 4(e),6(e)-tach coordinates with the substituents all in axial positions on the cyclohexane ring, the amines on one side of the ring and the methyl on the other. The complex $[Co(metach)_2]^{3+}$ exists as the *cis* and *trans* isomers, referring to the relative arrangement of the methyl groups. The *trans* isomer has a center of symmetry and is therefore achiral. The *cis* isomers possess only C_2 symmetry and exist as a pair of enantiomers, designated Δ and Λ. The chirality is defined by the skew pair of lines defining the pseudo D_3 axis and the line joining the two methyl groups. The $(-)_{589}$–$[Co(metach)_2]^{3+}$ isomer has been separated from a mixture of presumably the *cis* and *trans* isomers (*117*). On the basis of the CD spectrum of this complex it was tentatively assigned the Λ configuration.

3. *Macrocycles*

a. 1,4,7-Triazacyclononane (tacn). Tacn is constrained to coordinate facially. Since the $[Co(tacn)_2]^{3+}$ ion was first prepared (*118*), the chemistry of both the Co(II) and Co(III) complexes have been extensively studied by Wieghardt and co-workers (*102, 119, 120*). Only one isomer is possible for the $[Co(tacn)_2]^{n+}$ complexes. The conformational interchange of the linked five-membered rings is expected to be rapid for both the Co(II) and Co(III) complexes, the linking of the chelate rings in such a manner forces all the chelate rings of a particular tacn ring to assume the same conformation. The solid state structure is not known for the Co(III) complex, although it has been assumed to be similar to the $[Co(metacn)_2]^{3+}$ (*120a*), (*vide infra*). The X-ray crystal structure of the $[Co(tacn)_2]^{2+}$ complex shows both ($\lambda\lambda\lambda$,$\lambda\lambda\lambda$) and ($\delta\delta\delta$,$\delta\delta\delta$) conformers (referring to the conformations of each ring within each macrocycle) in the unit cell, but no mixed conformations ($\lambda\lambda\lambda$,$\delta\delta\delta$) were observed (*120*).

b. 2-Methyl-1,4,7-triazacyclononane (metacn). The presence of the methyl group on the tacn ligand dictates the conformation of all three linked chelate rings, since the complex is strongly destabilized by the presence of the methyl group in an axial position. Therefore (*R*)-metacn forms conformers with λ rings and (*S*)-metacn, δ. The possibility now exists for geometrical isomerism, although no isomers were separated in the study by Mason and Peacock (*121*). An X-ray structure of [Co(R--metacn)]$^{3+}$, most likely on a mixture of all possible isomers, is disordered with respect to the positions of the methyl groups (*122*). The structure does show, however, that the methyl groups are equatorially oriented and that the chelate rings are all in the λ conformation. Interestingly, the two ligands are rotated 7.6° toward a trigonal prismatic structure much like the tris-bidentate, although the two triangular faces are no longer linked. The most probable explanation is that the twist relieves some inter-ligand repulsion.

c. 1,4,7-Triazacyclodecane (tacd). The $[Co(tacd)_2]^{3+}$ complex was first prepared by Koyama and Yoshino (*118*). Two isomers are possible for this complex, *cis* and *trans* defining the relationship between the six-membered rings (Fig. 7). These isomers have been studied by Searle

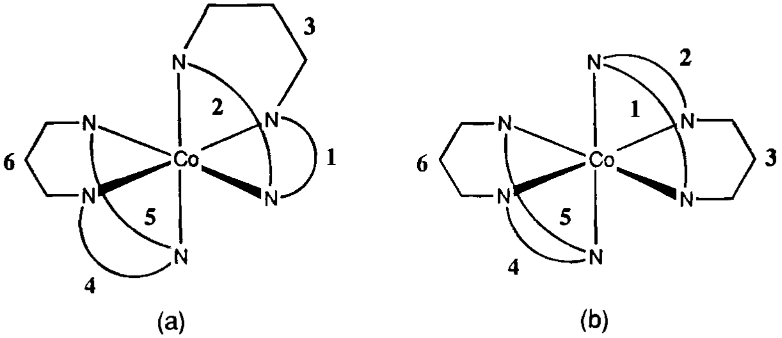


FIG. 7. The (a) *cis* and (b) *trans* isomers of $[Co(tacd)_2]^{3+}$.

and co-workers (*123, 124*). The *trans* : *cis* ratio under conditions where ion association is insignificant is 96 : 4. In the presence of PO_4^{3-} ion at 80°C the *cis* isomerized completely to the *trans*. The *cis* isomer is asymmetric, the absolute configuration being defined as Δ or Λ depending on the skew relationship between the lines joining the nitrogens of each six-membered ring. The enantiomers remain to be separated. A molecular mechanics study of the isomers and conformers of $[Co(tacd)_2]^{3+}$ predicted that for the *trans* isomer there would only be two conformations significantly populated in solution, both having the tn rings in the chair conformation. The predominant form has the conformation (λ,δ,chair) (λ,δ,chair) (in the order of numbering shown in Fig. 7) and the less stable conformer, which was estimated to represent probably only 1% of the total, (λ,δ,chair) (δ,δ,chair). The solution ^{13}C NMR is consistent with either 100% $(\lambda,\delta,\text{chair})_2$ conformation that has C_{2h} symmetry or a rapid equilibrium between the conformers. The *cis* isomer is predicted to have several conformations of similar strain energy, the most stable being $(\lambda,\delta,\text{chair})_2$, next the (λ,δ,chair) (δ,δ,δ-skew boat), and the only other possibility being (λ,δ,chair) (δ,δ,chair). ^{13}C NMR of the *cis* isomer gives a spectrum consistent with C_2 symmetry, but only the $(\lambda,\delta,\text{chair})_2$ has this symmetry. It seems likely, therefore, that the system is conformationally labile on the NMR time scale.

D. SEXADENTATE LIGANDS

1. *Linear Amines*

a. 1,14-Diamino-3,6,9,12-tetraazatetradecane (linpen). Linpen, (linear pentaethylenehexamine) can wrap around a metal ion in a variety of ways. Yoshikawa and Yamasaki (*125*) have pointed out that there are four geometrical isomers of the complex [Co(linpen)]$^{3+}$. However, if the absolute configuration of the nitrogens are included, eight energetically distinct isomers are possible, as shown in Fig. 8. The nomenclature system proposed (*96*) to describe this system is as follows: Consider the linpen molecule to be composed of dien fragments; starting at one end of the coordinated linpen and proceeding sequentially, there are four dien units in the molecule. Consider each dien unit in turn, and assign it either the *fac* (f) or *mer* (m) geometry. Thus in Fig. 8 structure A is ffff (f_4) and B is $f_2$mf or fmf_2, depending on which end is chosen as the beginning. Add to this the configuration of the secondary nitrogens, which may (at the central N in a *mer* fragment) be either *R* or *S*, and the structure of the isomer is defined. The eight possible isomers therefore are f_4-*RSSR*, $f_2$mf-*RSRS*, $f_2$mf-*RSSS*, fm_2f-*SRRS*, fm_2f-*SSSS*, mf_2m-*RRRR*, mf_2m-*RRRS*, and mf_2m-*SRRS*. In addition there are enantiomers for all of these complexes. In some cases conformational isomers are possible, although, as is usually the case for "en" rings, the equilibria between the various conformers is expected to be rapid. Yoshikawa and Yamasaki (*125*) have separated seven isomers of [Co(linpen)]$^{3+}$ and resolved them into enantiomeric pairs. Two of the isomers ($f_2$mf-*RSRS* and $f_2$mf-*RSSS*), differing only in the configuration at a single nitrogen, were not completely separated, because the racemization at that center was relatively rapid. The assignment of the structures was made on the basis of their ^{1}H NMR spectra and the

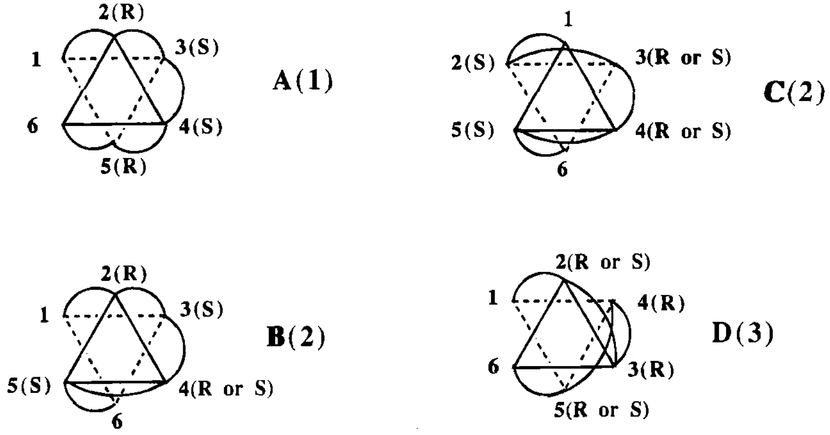


FIG. 8. The geometric isomers of [Co(linpen)]$^{3+}$; the configuration of the central amine nitrogen in a *mer* fragment (see text) is variable. This results in further isomers; the number of possibilities is given in parentheses.

facility of interchange between isomers differing only in the configuration at the N centers, that is, within one for the groups A to D in Fig. 8. The absolute configurations were assigned on the basis of the sign of the dominant transition in the CD in the region of the first absorption band. The assignment of one of the structures (f_4-*RSSR*) was later confirmed by X-ray crystallography (*126*). A molecular mechanics study of the [Co(linpen)]$^{3+}$ system (*96*), although not successfully reproducing product ratios for this complex system, was able to reasonably reproduce the structure of the f_4-*RSSR* complex determined by X-ray crystallography (*126*). Although the possibility of conformational isomerism was discussed in this study (*96*), it seems to have been ignored in the molecular mechanics study, where only one conformer (not necessarily the least strained) represented each isomer.

b. 1,16-diamino-3,7,10,13-tetraazahexadecane (dtah). The complex [Co(dtah)]$^{3+}$ appears to be a single isomer of C_1 symmetry judging by its ^{13}C NMR spectrum. The complex is therefore one of six possible isomers with the *cis* arrangement of the tn rings. The observation of a single isomer for the complex indicates that, unlike linpen, the coordination of dtah is highly stereospecific (*123, 124*).

2. *Branched Amines*

a. 1,4,7-tris(2-aminoethyl)-1,4,7-triazacyclononane (taetacn). Taetacn forms a single stereoisomer on coordination to Co(III); no others are possible (*128*). The complex is resolvable into enantiomers Δ and Λ describing the "(en)$_3$" portion of the molecule. A complete description of the structure can be given, for example, by Δ(λ,δ), where the first lower-case greek letter (λ) refers to the conformation of the five-membered rings in the tach moiety and the second (δ) refers to the conformation of the en rings. If necessary, the nomenclature could be extended to include different conformations within each group of rings, but this is not required. Molecular mechanics calculations on [Co(taetacn)]$^{3+}$ predicted that the Δ(λ,δ) comformer would be the most stable (*127*). This gives the *ob* conformation of the en rings, the *lel* conformation apparently being destabilized by the fusion of the en rings onto the tacn moiety. The conformation with *lel* rings is calculated to be 50 kJ mol^{-1} higher in energy than the *ob* conformation. A crystal structure of the complex shows the Δ(λ,δ) conformer, as predicted (*127*). An interesting feature of this crystal structure, although not discussed in the original text, is the observation that the ClO_4^- ion H-bonds to the C_3 face (opposite the macrocyclic face) in the manner commonly observed for PO_4^{3-} and other oxo-anions with 3-fold symmetry (*39*). The energy-minimized structure reproduces fairly well the observed structure, with the exception of the unusually long Co–N bond lengths for the primary amines [2.009(4) Å]. The prediction that the *lel* conformations will be high in energy and that the alternate tacn conformation $\Delta(\delta,\delta)$ will be 22 kJ mol^{-1} higher than the observed structure led these workers to predict that the observed conformer would be rigid in solution. In keeping with this, but not proving it, is the observation that the ^{13}C NMR indicates C_3 symmetry (*128*).

b. 1,4,7-tris(3-aminopropyl)-1,4,7-triazacyclononane (taptacn). The coordination geometry of the complex is a slightly distorted octahedron with the six-membered rings in the chair conformation (*129*). The complex is elongated along the 3-fold axis and the trigonal twist is very minor. The pattern of Co–N bond lengths shows a reverse trend to that observed for $[Co(taetacn)]^{3+}$; the primary amines have shorter Co–N bond lengths than the tertiary amines.

c. N,N,N',N'-tetrakis-(2-aminoethyl)-1,2-diaminoethane (tae-en). Tae-en, the amine analogue of edta, also called penten, originally synthesised and studied by Schwarzenbach et al. (*130, 131*) is able to form only a single geometric isomer when acting as a sexadentate ligand coordinated to the Co(III) ion. It exists as a pair of enantiomers. Its absolute configuration was determined by Muto et al. (*132*). The X-ray structure established that the $(+)_{589}$–$[Co(tae\text{-}en)]^{3+}$ complex is the $\Lambda\Delta\Lambda$ (or just Λ) isomer, in agreement with the predictions by Gollogly and Hawkins (*133*) and Yoshikawa et al. (*134*) but in contrast to the assignments made by Emmenegger and Schwarzenbach (*131*) and Mason and Norman (*135*). The chirality of the complexes is described as recommended by IUPAC (*16*). Each skew pair of chelate rings is assigned as either Δ or Λ. In these complexes there are three skew pairs of rings. The ligand forms a distorted octachedral array around the Co(III) ion. All of the chelating angles are less than 90°; however, the chelate angle formed between the tertiary amines nitrogens is significantly larger (89.5°) than the others. The bond lengths for the tertiary amines [1.96(2) Å] are shorter than for the primary amines.

d. N,N,N',N'-tetrakis(2-aminoethyl)-1,2-diaminopropane (tae-pn). The related complex (tae-pn) with a methyl substituent on the central en ring coordinates in a stereospecific fashion (*133, 136*). The X-ray structure (*136*) of the complex shows that *R*-tae-pn coordinates with the methyl group equatorially oriented, as is usual for chelate ring substituents, and with the overall configuration $\Delta\Lambda\Delta$ (Δ). The configuration of the pn group dictates the configuration of the whole complex. The conformation of the rings is in agreement with that predicted by molecular mechanics (*137*). The structure of the complex ion is similar to that of [Co(tae-en)]$^{3+}$.

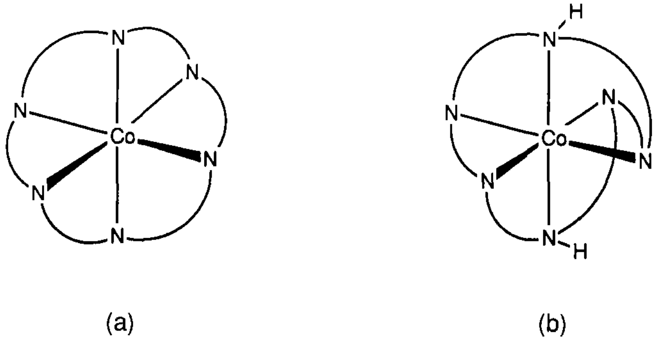
e. N,N,N'N'-tetrakis(2-aminoethyl)1,3-diaminopropane (tae-tn) and N,N,N'N'-tetrakis(2-aminoethyl)2,4-diaminopentane (tae-ptn). The tae-tn complex exists as an enantiomeric pair; the X-ray structure of the racemate is known (*138*). The tn ring has the skew boat conformation. The *RR*-2,4-pentanediamine analogue of tae-tn (*RR*-tae-ptn) coordinates stereospecifically with the λ-skew boat conformation of the backbone, with spectral properties similar to that of [Co(tae-tn)]$^{3+}$, and with both methyl groups equatorially disposed. The overall configuration is specifically directed to Δ by the requirement for the λ conformation of the "backbone" (*138*). The complex of *RS*-tae-ptn is required to adopt the chair conformation if both methyls are to be equatorial, as observed in the crystal structure (*138*). These three complexes with six-membered chelate rings as the "backbone" of the ligand have rather different structural features to the complexes of five--membered ring derivatives. For all of the complexes the mean Co–N bond lengths to the tertiary amines were longer than the average of the primary amines, and the chelate angles for the six-membered ring were all much greater than 90°; whereas the five-membered rings display rather typical values.

f. 1,1,1-Tris((2-aminoethyl)aminomethyl)ethane (sen). Only one stereoisomer is possible for complexes of sen. The crystal structures of both enantiomers of [Co(sen)]$^{3+}$ as the mixed chloride-(*d*)-tartrate salts (*139, 140*) are almost identical with respect to the structure of the complex ion (as they would be expected to be in the absence of crystal packing forces and the influence of the chiral anion): both have lel_3 arrangement for the $(en)_3$ portion of the molecule. Some strain is observed in the "capping" region of the molecule, the tetrahedral angles at the carbons of the cap and the adjacent amines being distorted (*139*). The "$(en)_3$" part of the molecule is very similar to the structure of $[Co(en)_3]^{3+}$; Co–N 1.971(6) Å, chelate angle 86.1(.2)°, indicating that the capping does not have a great effect on the geometry of the coordination sphere.

g. 1,1,1-Tris((3-aminopropyl)aminomethyl)ethane (stn). Stn is an analogue of sen with the en bridges replaced by tn bridges; the molecule coordinates in a manner similar to sen (*141*). In the solid state the tn rings are in a flattened chair conformation (*142*). The effect of the larger rings is to dramatically increase the Co–N bond lengths for all the bonds, even relative to $[Co(tn)_3]^{3+}$, and the chelate bite angle is increased to 94.5° (*142*). The lengthening of the bonds is associated with some relief of the strain in the cap region.

3. *Macrocylic Amines*

a. 1,4,7,10,13,16-hexaazaoctadecane (18N6). 18N6 is a macrocyclic analogue of linpen. 18N6 can form fewer isomers when coordinated to Co(III). The possibilities are restricted to those shown in Fig. 9. The complexes may be considered as being composed of two "$(en)_3$" moieties, with each alternate five-membered ring contributing to alternate "$(en)_3$" complexes. The first structure, which has the "all facial" (*fac*) arrangement, is composed of one Δ and one Λ $(en)_3$ group and has a center of symmetry; it is therefore achiral. The second isomer has the *mer* structure and is "composed" of two $(en)_3$ units of the same configuration. The *mer* structure has a second source of asymmetry, defined by the relative orientation of the two N–H bonds of the amine groups in the center of the *mer* fragments. This asymmetry is analogous to that observed for the enantiomers of *mer*-$[Co(dien)_2]^{3+}$ (i.e., δ-NH and λ-NH) (*101, 92*). Hay et al. (*143*) observed only a mixture of *mer* isomers in their study of this system; however, Yoshikawa (*144*) and Royer et al. (*145*) have separated the three isomers of $[Co(18N6)]^{3+}$. The *fac* isomer comprises less than one percent of the total and displays only a single line in the ^{13}C NMR spectrum, indicating, at least on average, D_{3d} symmetry. The two *mer* diastereomers have been resolved by Royer et al. (*145*). The resolved complexes racemize even in slightly acidic solution, and it was not possible to crystallize the optically active salts. The X-ray crystallographic structure of the racemic form of one of these



(a) (b)

FIG. 9. The geometric isomers of $[Co(18N6)]^{3+}$; (a) *fac*; (b) (δ-NH)(ΛΛ) *mer*.

diastereomers shows it to be the *mer*-(λ-NH) (ΔΔ) $[Co(18N6)]^{3+}$ complex and its enantiomer (*145*). The structure observed for this cation is in good agreement with that predicted by molecular mechanics (*144*). The complex may be considered to be similar to the *mer*-$[Co(dien)_2]^{3+}$ complex, and like that complex the crystal structure shows that the central Co–N bond in each of the *mer* sectins is shortened to 1.947(5) Å whereas the other bonds are slightly longer than normal for five-membered rings. The crystal structure (*146*) of the *fac* complex has S_6 symmetry, in agreement with that predicted by molecular mechanics (*144*), although in solution a single ^{13}C NMR resonance indicates D_{3d} symmetry, suggesting that the complex is probably undergoing rapid interconversion between two equivalent S_6 structures (*146*).

b. Tricyclohexyl18N6 (TC18N6). Royer et al. (*146*) have studied the complexes formed by TC18N6. The cyclohexanediamine used in the synthesis of this complex was the pure *RR* isomer; therefore, any chelate rings formed by this portion of the ligand are required to be in the λ conformation. In general the complexes formed by this ligand are more strained and less stable than their 18N6 analogues. Several isomers were isolated and given tentative structural assignments. Because of the uncertainty in the assignments and the rather unusual nature of the ligand, this system will not be discussed further.

c. 1,4,7,11,14,17-Hexaazacycloheneicosane (20N6). Only one isomer of $[Co(20N6)]^{3+}$ was formed out of the six geometrically distinct isomers possible. On the basis of the ^{13}C NMR several isomers could be eliminated. The spectra showed seven reasonances, consistent with a single isomer of C_2 symmetry. A molecular mechanics study (*147*) of some of the more likely conformers, in agreement with experiment, predicted that one isomer of C_2 symmetry would predominate in solution, being more than 14 kJ mol^{-1} more stable than any other isomer.

d. 1,4,8,11,15,18-Hexaazacycloheneicosane (21N6). The $[Co(21N6)]^{3+}$ complex, like the complex of 20N6, apparently consists of a single isomer with a simple three-line ^{13}C NMR spectrum indicating D_3 symmetry (i.e., the all-*fac* geometry) (*145*), the same connectivity as the *fac* 18N6 complex (see Fig. 9). The complex could be resolved into optical isomers, although the resolved complex racemized before suitable crystals could be grown for X-ray analysis. A crystal structure (*145*) of the isomer that crystallized out of the solution was one of the *mer* isomers with symmetry C_2 (the structure shown in the paper is incorrectly labeled and should read $\Lambda_5(\delta\delta\delta)\Lambda_6(\text{chair})_3$ *mer RR*). The structure of the complex shows a very large variation of the Co–N bond lengths, from 1.913(5) to 2.021(5) Å, which seems unrealistic. The structure also suffers from disorder in the ClO_4^- counter ions; consequently, no meaningful conclusions can be drawn from the published structural data. The ^{13}C NMR of the complex in solution, however, is incompatible with the observed crystal structure, which implies that a minor component of the solution has crystallized.

e. 1,2-bis(1,4,7-triaza-1-cyclononyl)ethane (dtne). Dtne is a bimacrocyclic ligand, consisting of two tacn ligands joined by an ethyl link between two amines. Each tacn moiety is constrained to coordinate facially, and thus the (mono) Co(III) complexes of dtne are limited to a single isomer (*148*). Also, the propyl-bridged bis-tacn (dtnp) has been synthesized, although like dtne no structural data have been reported for the Co(III) complex (*148*).

f. 6,14-diamino-6,14-dimethyl-1,4,8,11-tetraazacyclotetradecane (diamcyclam). The Co(III) complex of this ligand displays rather unusual spectral and redox properties, as will be discussed in later sections. The structure of the complex in the solid state shows considerably shortened Co–N bond lengths for all the bonds, with a mean for the macrocyclic ring of 1.938 Å and for the axial amines 1.946 Å (*149*). The complex is rather reminiscent of the $[Co(tamp)_2]^{3+}$, which it would become if the two en bridges were removed from the macrocycle. The shortening of the bond lengths is also observed in a similar structure, $[Co(tap)_2]^{3+}$, where the central amine in the complex is at a distance of 1.942(2) Å from the cobalt ion (*109*), suggesting that the 1,2,3-triamine structure is the crucial element in shortening of the Co–N bonds.

g. 1,8-diamino-1,8-dimethylamino-4,12-dimthyl-3,6,10,13-tetraazacyclotetradecane (diammecyclam). This ligand has an identical framework to diamcyclam and differs only in the substitutents (*150*). The mean Co–N bond lengths are longer than for diamcyclam, indicating that the substituents, methyl groups on the "en" rings and aminomethyl groups on the "tn" ring, have a significant effect on the bond lengths (*150a*). The effect is also observed in solution: *Dq* is lower and the reduction potential is more positive than for $[Co(diamcyclam)]^{3+}$.

4. Cage Complexes

The symmetrical cage complexes studied by Sargeson and co-workers have the general structure shown in Appendix I. There are many derivatives of this type of complex, mostly with substituents replacing the protons on the tertiary carbon of sar. Most will not be covered in this chapter, since they properly form the basis for a complete review in themselves. The basic sep and sar cages will be considered, and the derivatives will be included where particularly illuminating.

Several other encapsulating ligands have been synthesized using similar strategies and the $[Co(taetacn)]^{3+}$ and $[Co(tame)_2]^{3+}$ as substrate complexes.

a. Sepulchrate (sep). The complex $[Co(sep)]^{3+}$ is produced in a template reaction involving $[Co(en)_3]^{3+}$, formaldehyde, and ammonia in aqueous solution. The most striking property of this complex is that even the Co(II) complexes are inert, not exchanging metal ion with radioactive $^{60}Co^{2+}$ over a period of one day. Even more surprising is the fact that resolved $[Co(sep)]^{2+}$ is not racemized after two hours in solution (*6, 151*). The X-ray crystal structure of both the Co(III) (*151, 152*) and Co(II) (*6*) complexes are known. All three structures have approximate D_3 symmetry, with the en rings in the *lel* conformation in both oxidation states.

b. Sarcophagine (sar). $[Co(sar)]^{3+/2+}$ and its derivatives (*7*) have many properties similar to $[Co(sep)]^{3+/2+}$ complexes, mainly relating to the kinetic inertness of the complexes in both oxidation states and the relatively rapid rate of electron self-exchange. The structure of a sar derivative complex $[Co(diNOsar)]Cl_3 \cdot 2H_2O$ has the lel_3 conformation (*153*), although a molecular mechanics study predicted that the ob_3 would be the most stable (*7*). The ob_3 structure was observed however for the $[Co(diNOsar\text{-}H)]^{2+}$ complex, where deprotonation of one of the coordinated amines has occurred (*7*), and also for the hydroxylamine-capped complex (*154*). A comparison of the CD of the resolved $[Co(diAmsar)]^{3+}$ with that of the lel_3 $[Co(diAm\text{-}pnsar)]^{3+}$ is strongly indicative of $[Co(diAmsar)]^{3+}$ having the lel_3 conformation in solution (*150*).

c. (tacnsar). A capping reaction on $[Co(taetacn)]^{3+}$ with formaldehyde and nitromethane yields the $[Co(NOsartacn)]^{3+}$ complex (*128*). The X-ray crystal structure of the Λ complex (describing the "en_3" portion of the molecule) has the (δ,λ) conformation; that is, the "tacn" rings are in the δ conformation and the "en_3" rings are λ (*127*). This gives the ob_3 conformation to the complex. Molecular mechanics on the system concluded that, like the taetacn complex, the ob_3 conformation is by far the most stable (*127*).

d. (captame). Treatment of $[Co(tame)_2]^{3+}$ with formaldehyde and nitromethane yields a variety of distorted hexaamine complexes. One of these, captame (*155*), has been studied by X-ray crystallography. The complex, possessing six chiral N centers, could display up to 2^6 diastereomers, yet only a single diastereomer is observed. This complex is of interest here because of the reduced size of the cavity available to the cobalt ion.

III. Structure and Kinetic Stability

A. HYDROLYSIS

Hydrolysis of cobalt(III) amine complexes occurs by two routes. One route is pH-independent, which is usually measured in acidic conditions and is thus often termed acid hydrolysis or aquation. The second route, base hydrolysis, is usually first order in hydroxide ion and complex concentration, although under certain conditions the reaction may become independent of $[OH^-]$ or dependent on the general base (*156*).

Acid hydrolysis is much slower than base hydrolysis for these compounds. Base hydrolysis of cobalt(III) amine complexes is generally considered to occur by the $S_N1(CB)$ mechanism (*156*). This mechanism frequently involves deprotonation of a coordinated amine to generate the conjugate base (CB), followed by rate-limiting bond cleavage of a different Co–N bond. The deprotonation is thought to enhance the rate of Co–N bond cleavage at the other positions. This mechanism gives a rate law that is first order with respect to both hydroxide ion and complex ion concentration if pH of the measurements is significantly less than the pK_a of the coordinated amine. The observed second-order rate constant is then actually a composite of the deprotonation constant and the rate of dissociation of the ligand from the deprotonated complex. The pK_as of amines coordinated to Co(III) are not often known, although they are generally much greater than 13; therefore, most often an overall second-order reaction is observed. In cases where the kinetic measurements are made at a pH much greater than the pK_a, the rate of the base hydrolysis reaction can be independent of pH and the rate observed is the rate of Co–N bond cleavage.

Cobalt(III) hexaammine is quite inert to hydrolysis. In strongly basic media ($[OH^-] = 0.1$ to 2.1 M) the reaction rate increases and $[OH^-]$ apparently reaches a limiting value around 1 M, where the reaction becomes independent of $[OH^-]$, $\sim 3 \times 10^{-4}\ s^{-1}$ at 61.8°, $\mu = 2.0$ (*157*). The mechanism of the reaction involves the $S_N1(CB)$ pathway. The limiting rate observed at high pH is thought to reflect a pre-equilibrium ion pair formation between the complex ion and OH^-, rather than the first-order reaction of the fuly deprotonated complex ion. The rate of acid hydrolysis is not known, although (and probably because) it is exceedingly slow.

Cobalt(III) hexakismethylamine is prone to hydrolysis in neutral or slightly basic aqueous solution (*158*). For the corresponding chloropentaamine complexes (*159*), an increase of some 10^5 was observed in the rate of base hydrolysis of $[Co(NH_2Me)_5Cl]^{2+}$ compared to that of $[Co(NH_3)_5Cl]^{2+}$. The difference was attributed to steric effects and pointed to a dissociative type of mechanism for the hydrolysis, consistent with an $S_N1(CB)$ path. Similar arguments may be employed for the reactivity of the hexaamines.

$[Co(en)_3]^{3+}$ is inert to substitution in neutral and acidic aqueous solution up to 100°C (*160*). Reaction with the hydroxide ion in the absence of heterogeneous catalysts occurs at reasonable rates only above 70°C. Friend and Nunn (*160*) studied the hydrolysis of this complex in basic conditions, at 80°C ($\mu = 0.5$); the reaction is first order in $[OH^-]$ and $[Co(en)_3{}^{3+}]$, with a second-order rate constant of $(5 \pm 1) \times 10^{-4}\ M^{-1}s^{-1}$. Assuming the activation parameters apply at 25°C, the rate constant at that temperture would be $\sim 3 \times 10^{-9}\ M^{-1}s^{-1}$, that is, a half-life of around 14 years in 0.5 M NaOH.

The hydrolysis of $[Co(en)_3]^{3+}$ with NaOH in the presence of charcoal has an apparent rate constant of $\sim 5 \times 10^{-4}\ M^{-1}s^{-1}$ ($\mu = 1.0$) at 25°C (*161*); that is, the catalyst enhances the reaction some 10^5-fold. The catalytic efficiency is not the same for all types of charcoal, however. Like $[Co(NH_3)_6]^{3+}$, the rate of acid hydrolysis is exceedingly slow.

Very few other studies have been carried out on the hydrolytic reactivity of tris-bidentate complexes. In some instances it is noted that the complexes are prone to decomposition in basic solution. This applies to strained complexes such as those with seven-membered rings (*89*) or complexes with many axially disposed substituents (*162*).

The rate of hydrolysis of $[Co(tmen)_3]^{3+}$ (*162*) demonstrated the effect that steric crowding, in particular the presence of six axially oriented methyl groups, has on the reactivity of the $Co{-}N_6$ core. The rate of hydrolysis is first order with respect to base and complex, with an overall rate constant of $5\ M^{-1}s^{-1}$ at 25°C ($\mu = 1.0$) in the pH range 8–13. The reaction proceeds in a single observable step, to yield $[Co(tmen)_2(OH)_2]^+$. The reaction is consistent with a $S_N1(CB)$ mechanism (*162*) and is some nine orders of magnitude greater than estimated for $[Co(en)_3]^{3+}$ (*vide supra*).

In the bis-tridentate group of complexes, $[Co(dpt)_2]^{3+}$ is sensitive to hydrolysis in neutral aqueous solution, in contrast to *mer*-$[Co(dien)_2]^{3+}$, its five-membered ring analogue, but is stable in acidic solution (*104*).

Mention should be made of the special kinetic and thermodynamic stability observed for the sexadentate cage complexes, Sep, Sar, and their derivatives. It has proved impossible to dissociate Co(III) from these cages (*6,7*), extreme conditions being required even to remove the Co(II) ion from the cage (*163*).

B. RACEMIZATION

Δ-$[Co(en)_3]^{3+}$ is not racemized in the presence of OH^- at high temperatures; the observed loss of optical activity is associated with the formation of *cis* and *trans* $[Co(en)_2(OH)_2]^+$ (*164*). This is in keeping with the observation that *cis*-$[Co(en)_2en(OH)]^{2+}$ (i.e., with one monodentate en ligand) in basic aqueous solution does not cyclize to form $[Co(en)_3]^{3+}$ (*165*). In the presence of a large excess of free en, however, racemization is observed; the rate is dependent on en concentration, and the complex exchanges ligands at about the same rate as racemization (*164, 166*). Carbon black catalyzed racemization follows the rate law; $\nu = k_1[Co(en)_3{}^{3+}]_{ads}[OH^-]_{ads}$, where the concentrations refer to the amount of reactant adsorbed onto the surface of the catalyst, k_1 has a value of $(9 \pm 1) \times 10^{-4}$ $M^{-1}s^{-1}$ at 25°C (*167*). An effect of [en] was observed but was attributed solely to the pH of the basic amine. The reaction on the surface of the catalyst was proposed to occur via the $S_N1(CB)$ mechanism.

Λ-$[Co(en)_3]^{3+}$ is reported to resist racemization in refluxing 0.1 M HCl even in the presence of charcoal for 24 hours (*168*).

The racemization of $[Co(tmen)_3]^{3+}$ (*162*) is first order in hydroxide ion and complex; however, unlike $[Co(en)_3]^{3+}$, the rate constant is two orders of magnitude greater than that observed for its hydrolysis, 6.9×10^2 $M^{-1}s^{-1}$ in the pH range 6 to 9 ($\mu = 1.0$, 25°C) (*169*). Since the rate determining step in the hydrolytic path (the dissociation of one end of a tmen ligand from the deprotonated complex) would be the same for the racemization if it went via a bond-cleavage path, the racemization cannot proceed via this route. Since the reaction does not proceed with Co–N bond cleavage, it must go via some type of twist mechanism, the most likely being the trigonal twist where the reaction goes via a trigonal prismatic transition state (*170*). This route is favored for $[Co(tmen)_3]^{3+}$, since the ground state structure is already trigonally twisted by 16° toward the trigonal prismatic structure. The OH^- dependence of the reaction suggests that the conjugate base of the complex is much more prone to racemization than the protonated species, as observed for $[Co(stn)]^{3+}$ (*vide infra*). The complex racemizes with a rate constant of about 10^{-8} s^{-1} in 0.1 M perchloric acid (*171*).

mer-$[Co(dien)_2]^{3+}$ has a pair of enantiomers that differ only in the configuration of a secondary amine (*91*). In acidic conditions it is possible to resolve these isomers. The racemization of the complexes is first order in [base] and [complex]. At 35°C, pH 7.42, the reaction has a half-life of 93 minutes (*91*). In contrast to this, *mer*-$[Co(dpt)_2]^{3+}$, having an analogous pair of enantiomers, is observed to invert the secondary amine in neutral to slightly basic solution at a rate that is rapid on the ^1H NMR time scale at room temperature (*104*). The pK_as of the coordinated secondary amines in the two complexes are not known and may differ somewhat; however, the difference in the rate of inversion of the two deprotonated amines is much greater than could be attributed to a difference in pK_a. Almost certainly this reflects the greater flexibility of the six-membered rings, allowing the attainment of the planar geometry at the deprotonated N center required for inversion.

The racemization of $[Co(stn)]^{3+}$ has been studied (*142*) in buffered solutions at elevated temperatures and found to be first order in $[OH^-]$; at 55°C the second-order rate constant was $2.9 \times 10^2\ M^{-1}s^{-1}$. The reaction is thought to involve deprotonation of one of the secondary amines followed by a trigonal twist where the three secondary amines are required to invert simultaneously with the inversion of the metal center. Another possibility, given that in many buffers the complex was observed to decompose, is that racemization occurs with considerable Co–N bond breakage. The corresponding experiments have not been performed with $[Co(sen)]^{3+}$, so the effect of the six-membered rings cannot be quantified.

The structure of the cages sep and sar is such that to invert the overall configuration of the complex, simultaneous inversion of all six coordinated secondary amines is necessary. This leads to the extraordinary configurational stability; even the Co(II) sar complex is not racemized in solution over 2 hours (*6, 7*).

IV. Spectroscopic Properties

A. LIGAND FIELD SPECTRA

The electronic structure, in particular the electronic spectroscopic properties, of the whole class of cobalt amine complexes may be reduced to a discussion of the central $Co–N_6$ core. This disregards, of course, the charge-transfer transition that in these compexes typically occurs around 250 nm. The geometrical structure is either octahedral or is defined in terms of a subgroup of the cubic point group O_h, where the symmetry of the complex ion depends on the denticity and molecular structure of a given ligand molecule. In most cases discussed here, the assumption of octahedral symmetry is a valid first approximation.

CoN_6 units in the oxidation state III are invariably low spin, that is, in the $t_{2g}{}^6$ configuration. Ligand field theory provides the appropriate theoretical model for dealing with optical spectra and related properties of these compounds. The appropriate Tanabe–Sugano diagram is shown in Fig. 10. The cobalt amine complexes fit into the right-hand part of this term diagram, and the transitions occur in the shaded region. The observed pattern of the two absorption bands in the UV/vis region are assigned to the two spin-allowed singlet-to-singlet transitions. Depending on the degree of distortion from octahedral symmetry, these absorption bands may be broadened owing to splitting of excited *T* states into two (or more) components. With a few exceptions the absorption maxima of $Co(III)N_6$ complexes are around 470 and 340 nm (21300 and 29400 cm^{-1}), producing the familiar orange-yellow color of these classical coordination compounds. Since the UV/vis spectrum of an octahedral or pseudo-octahedral $Co{-}N_6$ chromophore consists of only two spin-allowed absorption bands, it is not possible to extract all three ligand field parameters *Dq, B,* and *C*. It has become standard practice to fix the ratio *C*/*B* at a constant value, usually 4 or close to 4 (*172*). A

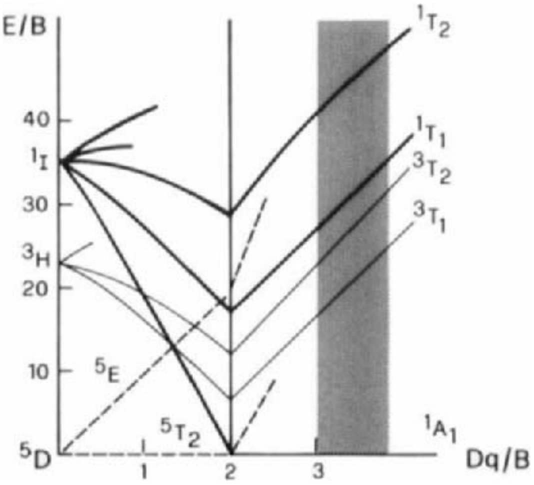


FIG. 10. A simplified Tanabe–Sugano diagram for d^6 octahedral metal ions: the states of spectroscopic interest for the cobalt(III) hexaamines. The *Dq*/*B* region in which these complexes lie is shaded.

straightforward numerical procedure for determining *Dq* and *B* from the two singlet-singlet bands has been described (*173*). *Dq* and *B* are on the order of 2300 and 600 cm^{-1}, respectively. Octahedral coordination for these low-spin d^6 compounds is characterized by the highest possible ligand field stabilization energy of 24 *Dq* units, or approximately 650 kJ mol^{-1}.

The spectral properties of the complexes under discussion are shown in Table II. The *Dq* values range from 2070 cm^{-1} for $[Co(1,4\text{-}me_2\text{-}dien)_2]^{3+}$ to 2390 cm^{-1} for $[Co(diamcyclam)]^{3+}$. Some general observations can be made: The most inert complexes have *Dq* values in the range 2280 to 2320 cm^{-1}. *N*-methylation of the ligands reduces the *Dq* value, as can be seen in comparing $[Co(NH_2Me)_6]^{3+}$ and $[Co(meen)_3]^{3+}$ to their unsubstituted analogues. The complexes of O_h symmetry $[Co(NH_3)_6]^{3+}$ and $[Co(NH_2Me)_6]^{3+}$ have significantly lower extinction coefficients than almost all the other complexes. The higher extinction coefficients of the other complexes is probably a consequence of deviation from local O_h symmetry, which may increase the strength of the vibrational-electronic coupling, the major contributor to the observed transition intensity.

Within the group of tris-bidentate complexes with 5-membered rings, $[Co(en)_3]^{3+}$ and C-substituted derivatives with one or two equatorially oriented methyl groups, all have *Dq* values in the region 2300 to 2310 cm^{-1}. There seems to be no effect on *Dq* of the conformation of the chelate rings; *lel* and *ob* pn and (±)-2,3-bn show essentially identical spectra. The complexes of the more substituted amines pen, dmbn, and chxn with equatorially oriented substituents have *Dq* values in the region of 2280 cm^{-1}, again with no dependence on the conformation of the ligand. Complexes with axially oriented methyl groups on the rings, such as the tris complexes in ibn, *meso*-2,3-bn, and tmen, all have significantly weaker ligand fields than observed for complexes with similar degrees of substitution (except tmen of course) but with equatorially oriented methyls. The only complexes with five-membered rings to show a dependence of *Dq* on ligand conformation were those of *RS*-meamcha, where the *ob* isomers have the stronger ligand field.

The group of tris-bidentate complexes with six-membered rings are similarly affected by ring substituent orientation. One major distinction between the complexes with five-membered rings and this class of complexes is that for the six-membered rings the conformation of the rings appears to have a significant effect on *Dq*. Thus, for example $[Co(tn)_3]^{3+}$ and C-methylated analogues where the chair conformation is possible, complexes of 1,3-bn and *RS*-ptn have *Dq* values in the region 2190 to 2210 cm^{-1}; but for $\Delta[Co(RR\text{-}ptn)_3]^{3+}$ the complex is forced into

TABLE II

ELECTRONIC PROPERTIES OF COBALT(III) HEXAAMINES

Ligands	Abs. spec.[a] nm(log ε)	Dq(cm^{-1}) B(cm^{-1})	$E_{1/2}$[b] vs. NHE	References
Monodentate ligands				
$(NH_3)_6$	474(1.76)	2278	−0.02	(*79,190*)
	339(1.67)	620		
$(NH_2Me)_6$	508(1.88)	2131		(*232*)
	360(1.88)	610		
$(NH_2OH)_6$	437(2.07)	2460		(*233*)
	318(2.3)	630		
Bidentate ligands				
Five-membered rings				
(en)$_3$	467(1.97)	2303	−0.17	(*89,190*)
	339(1.93)	590		
lel$_3$-(pn)$_3$	468(2.00)	2302	−0.13	(*37,190*)
	339(1.98)	590	−0.09[c]	(*39*)
lel$_2$*ob*-(pn)$_3$	468(1.98)	2300	−0.11[c]	(*37,39*)
	340(1.95)	590		
lelob$_2$-(pn)$_3$	469(1.95)	2300	−0.12[c]	(*37,39*)
	340(1.91)	590		
ob$_3$-(pn)$_3$	468(1.96)	2300	−0.13[d]	(*37,39*)
	339(1.91)	600		
lel$_3$-(±-2,3-bn)$_3$	465(2.00)	2314		(56)
	337(1.97)	600		
ob-(±-2,3-bn)$_3$	465(1.99)	2314		(*56*)
	337(1.96)	600		
fac-(ms-bn)$_3$	474(2.03)	2276		(*47*)
	340(1.99)	610		
mer-(ms-bn)$_3$	474(2.01)	2276		(*47*)
	340(1.97)	610		
mer-(ibn)$_3$	481(2.03)	2240		(*50*)
	347(2.00)	590		
fac-(ibn)$_3$	481(2.04)	2240		(*50*)
	347(2.00)	590		
(tmen)$_3$	504(2.25)	2140	+0.28	(*162*)
	362(2.25)	570		
(dap)$_3$	468(1.97)	2302		(*55*)
	338(2.10)	600		
mer-Λ-*lel*$_3$-(S-dmbn)$_3$	473(2.02)	2279		(*56*)
	342(1.99)	600		
fac-Λ-*lel*$_3$-(S-dmbn)$_3$	473(2.02)	2279		(*56*)
	342(1.99)	600		
mer-Δ-*lel*$_3$(R-pen)$_3$	472(2.10)	2277		(*56*)
	345(2.2sh)[d]	570		
fac-Δ-*lel*$_3$-(R-pen)$_3$	472(2.06)	2277		(*56*)
	345(2.1sh)[d]	570		
mer-Δ-*ob*$_3$-(R-pen)$_3$	472(2.07)	2277		(*56*)
	345(2.1sh)[d]	570		

(continued)

TABLE II (*Continued*)

Ligands	Abs. spec.[a] nm(log ε)	Dq(cm^{-1}) B(cm^{-1})	$E_{1/2}$[b] vs. NHE	References
fac-Δ-*ob*$_3$-(R-pen)$_3$	472(2.08) 345(2.3sh)[d]	2277 570		(*56*)
Δ-*ob*$_3$-(SS-dpen)$_3$	472(2.07) obscured by CT band			(*64*)
Δ*lel*$_3$-(SS-dpen)$_3$	472(2.10) obscured by CT band			(*64*)
lel$_3$-(chxn)$_3$	472(2.00) 342(1.97)	2281 590	−0.20	(*61,190*)
lel$_2$*ob*-(chxn)$_3$	473(2.01) 342(1.99)	2276 600		(*61*)
lelob$_2$-(chxn)$_3$	473(2.01) 342(1.99)	2276 600		(*61*)
ob$_3$-(chxn)$_3$	473(2.00) 343(1.97)	2275 590		(*61*)
fac-Δ-*lel*$_3$-RS-meamcha	481(2.11) 348(2.10)	2239 580		(*62*)
mer-Δ-*lel*$_3$-RS-meamcha	481(2.09) 354(2.07)	2244 610		(*62*)
mer-Λ-*ob*$_3$-RS-meamcha	478(2.09) 345(2.07)	2252 600		(*62*)
fac-Λ-*ob*$_3$-RS-meamcha	474(2.04) 345(2.03)	2269 580		(*62*)
Δ-*lel*$_3$-(RR-1,2-cptn)$_3$	493(1.80) 353(1.92)	2190 590		(*58*)
Δ-*lel*$_2$*ob*-(±-1,2-cptn)$_3$	495(1.90) 352(1.91)	2184 610		(*58*)
Δ-*lelob*$_2$-(±-1,2-cptn)$_3$	498(1.88) 353(1.93)	2173 610		(*58*)
fac,mer-(RS-1,2-cptn)$_3$	476(2.04) 344(2.02)	2262 600		(*59*)
(meen)$_3$	493(2.06) 351(2.01)	2194 610		(*66*)
Six-membered rings				
(tn)$_3$	490(1.88) 351(1.88)	2202 600	+0.13	(*89,182*)
fac-Δ-(S-1,3-bn)$_3$	490(1.93) 352(1.93)	2199 590		(*75*)
fac-Λ-(S-1,3-bn)$_3$	489(1.93) 352(1.94)	2203 590		(*75*)
mer-Δ-(S-1,3-bn)$_3$	491(1.92) 352(1.92)	2198 590		(*75*)
mer-Λ-(S-1,3-bn)$_3$	491(1.92) 352(1.92)	2198 590		(*75*)
Δ-*lel*$_3$-(RR-ptn)$_3$	482(1.88) 347(1.89)	2236 590		(*79*)
Λ-*ob*$_3$-(RR-ptn)$_3$	488(1.98) 350(1.96)	2212 600		(*79*)

(continued)

TABLE II (*Continued*)

Ligands	Abs. spec.^{a} nm(log ε)	Dq(cm^{-1}) B(cm^{-1})	$E_{1/2}{}^b$ vs. NHE	References
fac-Δ-(S-Phtn)$_3$	492(2.04)	2186		(*83*)
	357(2.35 sh)^d	560		
fac-Λ-(S-Phtn)$_3$	492(2.05)	2163		(*83*)
	357(2.4 sh)^d	590		
mer-Δ-(S-Phtn)$_3$	495(2.04)	2176		(*83*)
	357(2.34 sh)^d	570		
Λ-*ob*$_3$-(SS-dppn)$_3$	506(2.35)			(*84*)
	obscured by CT band			
Δ-*lel*$_3$-(SS-dppn)$_3$	493(1.92)			(*84*)
	obscured by CT band			
mer-Δ-(1R-2R-chxtn)$_3$	495(1.97)			(*85*)
	—			
fac-Δ-(1R-2R-chxtn)$_3$	489(2.09)			(*85*)
	—			
mer-Δ-(1R,2S-chxtn)$_3$	485(2.01)			(*85*)
	—			
mer-Λ-(1R,2S-chxtn)$_3$	485(1.97)			(*85*)
	—			
fac-Λ-(1R,2S-chxtn)$_3$	485(1.97)			(*85*)
	—			
mer-(ama)$_3$	514(2.14)	2100		(*88a*)
	365(2.10)	591		
Seven-membered rings				
(1,4-bn)$_3$	503(1.92)	2152		(*89*)
	357(1.87)	600		
Tridentate ligands				
mer-(dien)$_2$	463(2.16)	2315	-0.21	(*94,102*)
	341(2.03)	600	$+0.03^c$	(*186*)
s-*fac*-(dien)$_2$	459(1.82)	2345	-0.03^c	(*94,186*)
	333(1.81)	600		
u-*fac*-(dien)$_2$	465(1.97)	2312	-0.01^c	(*94,186*)
	338(1.95)	590		
(pet)$_2$	481(1.97)	2240	-0.13	(*102*)
	347(1.95)	590		
mer-(dpt)$_2$	512(1.94)	2116	$+0.28$	(*104,102*)
	361(2.08)	610		
s-*fac*-(medien)$_2$	481(1.90)	2250	-0.01	(*107,102*)
	340(1.95)	640	$+0.23^c$	(*186*)
s-*fac*-(etdien)$_2$	489(1.87)		$+0.01$	(*102*)
	—			
s-*fac*-(budien)$_2$	490(1.91)		$+0.02$	(*102*)
	—			
1,4-(me$_2$-dien)$_2$	524(2.19)	2073	$+0.26$	(*102*)
	365(2.15)	630		
(tap)$_2$	460(1.81)	2344	-0.34	(*102*)
	331(1.75)	620		
s-*fac*-(tamp)$_2$	457(1.83)	2350		(*111*)
	331(1.80)	610		

(*continued*)

TABLE II (*Continued*)

Ligands	Abs. spec.^{a} nm(log ϵ)	Dq(cm^{-1}) B(cm^{-1})	$E_{1/2}{}^b$ vs. NHE	References
u-*fac*-(tamp)$_2$	460(1.86)	2340		(*111*)
	331(1.80)	620		
(tab)$_2$	462(1.87)	2325	−0.31	(*102*)
	335(1.86)	610		
(tacn)$_2$	459(1.98)	2344	−0.41	(*102*)
	333(1.94)	600		
(R-me-tacn)$_2$	~463(1.93)	2317	−0.41	(*121,102*)
	~340(1.89)	570		
(tacd)$_2$	470(1.86)	2290	−0.29	(*102*)
	341(1.94)	590		
(tame)$_2$	472(1.91)	2276	−0.43	(*113,102*)
	345(1.88)	570		
(tach)$_2$	478(1.88)	2255		(*115*)
	342(1.88)	620		
cis-(metach)$_2$	479(1.89)	2249		(*117*)
	345(1.87)	600		
Sexadentate ligands				
f_4RSSR-linpen	472(1.93)	2286		(*125*)
	339(1.89)	610		
$f_2$mf-linpen^e	474(2.23)	2271	−0.15^f	(*125,102*)
	343(2.11)	590		
fm_2f-SRRS-linpen	462(2.16)	2323		(*125*)
	339(2.00)	570		
fm_2f-SSSS-linpen	469(2.33)	2291		(*125*)
	341(2.27)	590		
mf_2m-RRRR-linpen	473(2.25)	2276		(*125*)
	342(2.08)	590		
mf_2m-RRRS-linpen	476(2.31)	2264		(*125*)
linpen	342(2.18)	610		
mf_2m-SRRS-linpen	481(2.33)	2246		(*125*)
	344(2.18)	610		
mer-*cis*-dtah	485(2.04)	2223		(*123*)
	349(2.01)	590		
fac-18-N-6	480(2.33)			(*146*)
	—			
mer-18-N-6	485(2.32)			(*143,145*)
	—			
mer-20-N-6	485(2.04)	2219		(*123*)
	349(2.02)	600		
fac-21-N-6	508(2.37)	2130		(*145*)
	361(2.55)	600		
tae-en	488(2.33)	2223		(*134*)
	342(2.22)	660		
tae-pn	488(2.33)	2223		(*134*)
	342(2.23)	660		
tae-tn	476(1.96)	2260		(*234*)
	345(1.95)	590		

(*continued*)

TABLE II (*Continued*)

Ligands	Abs. spec.[a] nm(log ε)	Dq(cm^{-1}) B(cm^{-1})	$E_{1/2}$[b] vs. NHE	References
ΔΔΛ-RR-tae-ptn	481(2.07)	2239		(*234*)
	348(1.98)	580		
RS-tae-ptn	500(2.32)	2162		(*234*)
	356(2.20)	600		
tae-tmd	500(2.23)	2165		(*234*)
	353(2.11)	620		
taetacn	480(2.38)	2243	−0.12	(*128*)
	347(2.30)	590		
taptacn	497(1.89)	2168	−0.01	(*129*)
	358(1.97)	580		
sen	467(2.05)	2311	−0.30	(*235,190*)
	340(2.01)	580		
stn	495(1.91)	2182		(*141*)
	353(2.09)	600		
dtne	495(2.45)	2194	−0.02	(*102*)
	345(2.33)	670		
diamcyclam	451(1.60)	2386	−0.61	(*149*)
	327(1.62)	620		
diammecyclam	461(2.21)	2330	−0.38	(*150*)
	336(2.30)	590		
sep	472(2.04)	2284	−0.26	(*6,190*)
	340(2.06)	610		
sar	471(2.13)	2282	−0.40	(*7,190*)
	343(2.03)	580		
diNOsar	473(1.60)	2273	+0.04	(*7,190*)
	343(2.09)	590		
diClsar	473(2.16)	2271	−0.14	(*7,190*)
	344(2.08)	580		
fac-Δ-*lel*$_3$-diAmpnsar^{5+}	480(2.18)	2245	−0.30[g]	(*150*)
	346(2.13)	590		
fac-Δ-*ob*$_3$-diAmpnsar^{5+}	450(1.91)	2383	−0.62[g]	(*150*)
	331(1.97)	580		
NOsartacn	488(2.52)	2211	+0.06	(*128*)
	350(2.42)	600		
captame	470(2.53)	2287	−0.31	(*155*)
	342(2.62)	580		

[a] Absorbance spectra measured in aqueous solution.

[b] $E_{1/2}$ values in all solvents have been converted to NHE by adding +0.236 V to quoted SCE values.

[c] In acetone versus Ag/AgCl.

[d] sh, shoulder.

[e] Mixture of isomers.

[f] The structure of the complex was not specified; however, the quoted spectrum matches closely that reported for the $f_2$mf isomers.

[g] Redox potential reported for the 2+/3+ couple rather than for the protonated 4+/5+.

the *lel*$_3$ conformation and *Dq* increases to 2240 cm^{-1}. From these results it appears that the chair conformation is favored energetically over the *lel* skew boat in these cases, but the latter conformation gives the higher ligand field. For tris-bidentate complexes with six-membered rings the *ob* conformers give weaker ligand fields than *lel* conformers.

Bis-tridentate complexes follow similar trends to those previously discussed, namely, increasing ring size and substitution decreases *Dq*. A good example of the effect of ring size on the *Dq* value is in the series *mer*-[Co(dien)$_2$]$^{3+}$, *mer*-[Co(pet)$_2$]$^{3+}$, *mer*-[Co(dpt)$_2$]$^{3+}$, where *Dq* is 2320, 2240, and 2120 cm^{-1}, respectively. In the series s-*fac*-[Co(dien)$_2$]$^{3+}$, s-*fac*-[Co(medien)$_2$]$^{3+}$, [Co(1,4-me$_2$dien)$_2$]$^{3+}$ methyl substitution on the amines dramatically decreases the *Dq* values, 2350, 2250, and 2070 cm^{-1} respectively.

For the complexes of sexadentate ligands, the ring-size generalization holds in most cases, with the exception of the tetraaminoethyl substituted bidentate ligands, where the effect is modulated by the four five-membered rings attached to the diamine backbone. *Dq* increases going from [Co(tae-en)]$^{3+}$ (2220 cm^{-1}) to [Co(tae-tn)]$^{3+}$ (2260 cm^{-1}); in the first case the complex is severely strained as observed in the crystal structure (*132*); some of the strain is relieved by the larger ring in the second case (*138*). A comparison of *Dq* for [Co(en)$_3$]$^{3+}$ (2300 cm^{-1}), [Co(sen)]$^{3+}$ (2300 cm^{-1}), and [Co(sar)]$^{3+}$ (2280 cm^{-1}) demonstrates that the C_3 "capping" of the [Co(en)$_3$]$^{3+}$ moiety has only a small effect on the electronic structure of these complexes.

The caged [Co(pn)$_3$]$^{3+}$ complexes, *lel*$_3$ and *ob*$_3$ [Co(diAm-pnsar)]$^{3+}$, have a marked dependence of *Dq* on the conformation, the *lel*$_3$ complex has a typical value (2240 cm^{-1}), whereas the *ob*$_3$ complex is greenish-yellow and has a *Dq* of 2380 cm^{-1} (*150*). The capping of the faces of the complexes in this case leads to a dramatic increase in ligand field strength for the *ob*$_3$ complex.

All these observations can be rationalized on the basis of steric demands of the ligand set. The complexes with greater steric crowding have reduced ligand-field strengths, which is associated with a lengthening of the mean Co–N bond length. Ligands such as diamcyclam and the *ob*$_3$ conformer of diampnsar, which tend to compress the Co–N bonds, yield complexes with higher than typical ligand-field strengths. Figure 11 shows a plot of mean Co–N bond length versus ν_1, the energy of the first spin-allowed transition. This is a purely empirical relationship; however, it shows that indeed there is a significant effect of bond length on *Dq*. This effect has been noted previously (*102, 174*) although plotted differently. Those authors plotted *Dq* versus $1/r^5$ and $\lambda_{\max}$ versus r^6, respectively. While plots such as this may be theoretically signif-

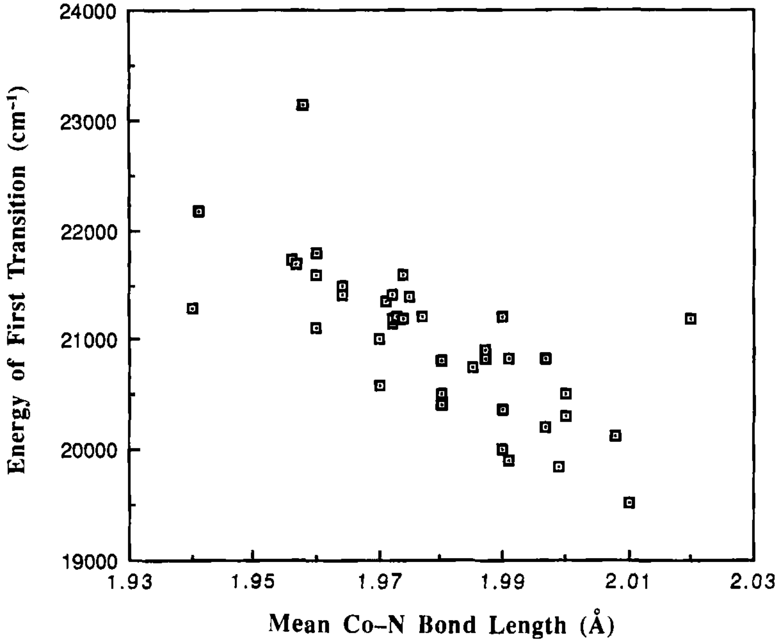


FIG. 11. Plot of the mean Co–N bond length (nm) versus the energy of the first spin-allowed transition ($^1A_1$ to $^1T_1$ of O_h parentage) (cm^{-1}). The data are from Tables I and II.

icant, the standard deviations in the bond lengths are so great that the plots are practically worthless.

Another factor that influences the electronic structure of the complexes is distortion from O_h symmetry of the donor atom positions. There seems to be a general trend toward higher extinction coefficients as the complexes are distorted away from octahedral symmetry. One measure of the distortion is the twist angle ϕ. The angle is defined for the tris-bidentate group of complexes in Fig. 5. This definition can be extended to include any complexes with a real or pseudo threefold axis, such as the bis-tridentates of *fac* symmetry and many sexadentates.

In terms of simple ligand-field theory the splitting of the *d* orbitals effected by the approach of the ligands along the *x*, *y*, and *z* axes should increase as the M–L distance is reduced. In molecular orbital terms, though, there should be an optimum M–L distance where orbital overlap is maximized; any change from this distance should decrease the strength of that bond. The question seems to be whether there is an optimal Co–N distance, reduction of which reduces rather than increases *Dq*. It has been observed for the relatively large Ni^{2+} ion that the value of *Dq* attributable to the equatorial ligand field reaches a maximum and then decreases when coordinated with progressively smaller N_4 macrocycles (*175*). The same authors speculate that this effect is not observed for Co(III) because the relatively small ion does not allow an octahedral array of amines to approach close enough to reach the point of maximum ligand–metal interaction. These authors predict that maximum ligand field strength will be observed when the Co–N equilibrium bond length is in the region of 1.92 Å. Interestingly, although not necesarily supporting this speculation, several groups of workers in the molecular mechanics field have found that a hypothetical "unstrained" Co–N bond length of this magnitude is required to correctly predict the observed bond lengths in crystal structures.

B. ^{59}Co NMR

^{59}Co has an abundance of ~100%, and its natural abundance detection sensitivity of 1572 relative to ^{13}C makes it rather facile to observe (*176*). However, it has a nuclear spin of 7/2 and a moderate quadrupole moment. The quadrupole moment makes the ^{59}Co line widths very sensitive to electric field gradients at the cobalt atom and therefore to the symmetry of the complex ion (*176*). A wide range of chemical shifts is observed for cobalt(III) complexes, from $[Co(CO_3)_3]^{3-}$, +14130 ppm, to $[Co(CN)_6]^{3-}$, 0 ppm (*176*). It was shown that there exists a linear correlation between the chemical shift of a Co(III) complex and the energy of its first *d-d* transition (ν_1) (*177*), as expected from the Griffith and Orgel (*178*) crystal field interpretation of the paramagnetic term for the shielding of the nucleus.

More recently it has been shown that in addition to ν_1 the nephelauxetic ratio β [$\beta = B/B_g$; B_g is the B value for the free ion in the gas phase and is equal to 1120 cm^{-1} for Co(III) (*173*)] has an effect on the shielding experienced by the cobalt nucleus. Juranic (*179, 180*) and Bramley et al. (*173*) found that there is a linear relationship between the chemical shift and $\beta \cdot \nu_1$. The correlation is rather good for cubic complexes (O_h symmetry of donor atoms) but does not hold as well for distorted complexes (such as the tris-chelates). ^{59}Co NMR data are shown in Table III.

^{1}H and ^{14}N NMR spectra of a series of pentaammine cobalt complexes

TABLE III

^{59}Co NMR DATA

Complex	δ (ppm)	Line width (Hz)	Reference
$[Co(NH_3)_6]^{3+}$	8100	220	(*236*)
$[Co(NH_2OH)_6]^{3+}$	6500	210	(*236*)
$[Co(en)_3]^{3+}$	7150	90	(*237*)
$[Co(pn)_3]^{3+}$ *ob*$_3$	6990	310	(*238*)
$[Co(pn)_3]^{3+}$ *mer lel*$_3$	7060	100	(*238*)
$[Co(pn)_3]^{3+}$ *fac lel*$_3$	7070	110	(*238*)
$[Co(chxn)_3]^{3+}$ *lel*$_3$	7330	90	(*150*)
$[Co(chxn)_3]^{3+}$ *ob*$_3$	7410	170	(*150*)
$[Co(tmen)_3]^{3+}$	8210[a]	550	(*162*)
$[Co(tn)_3]^{3+}$	8260	160	(*238*)
$[Co(RR\text{-}ptn)_3]^{3+}$ *lel*$_3$	8070	200	(*239*)
$[Co(RR\text{-}ptn)_3]^{3+}$ *ob*$_3$	8190	120	(*239*)
$[Co(1,4\text{-}bn)_3]^{3+}$	8670		(*240*)
$[Co(tame)_2]^{3+}$	7460		(*173*)
$[Co(tacn)_2]^{3+}$	6430		(*173*)
$[Co(sen)]^{3+}$	6800	360	(*150*)
$[Co(sep)]^{3+}$	6870	270	(*150*)
$[Co(sar)]^{3+}$	6800	280	(*150*)
$[Co(diAMsar)]^{3+}$	6790	780	(*150*)

[a] Measured versus $[Co(en)_3]^{3+}$ as a secondary reference.

has also been interpreted in terms of the electronic structure of the Co(III) complex (*181*). The chemical shifts followed the same trend as observed for the ^{59}Co NMR chemical shifts, indicating that the partially filled *d* shell is largely responsible for the variation.

V. Redox Properties

In general the extreme sensitivity of the whole class of cobalt(II) amine complexes toward dioxygen underscores their reducing character. A quantitative measure of this property is the reduction potential:

$$[CoN_6]^{3+} + e^- \rightleftharpoons [CoN_6]^{2+}; E^0 \tag{2}$$

Owing to the very facile substitution of the amine ligands in the reduced form of many of the complexes, electrochemical reversibility is very often not obtained. Electrochemical data thus are frequently limited to measurement of the reduction step. Nevertheless, reduction potentials are valuable quantities for discussing similarities and disparities within this class of compounds.

The published $E_{1/2}$ values for the complexes in question are shown in Table 2.

If $[Co(en)_3]^{3+}$ is taken as a reference complex for the tris-bidentate complexes, one observes that the "unstrained" complexes with five-membered rings have rather similar reduction potentials. The complexes of $[Co(pn)_3]^{3+}$, in acetone at least, become progressively easier to reduce with increasing *ob* content. The reduction potential of $[Co(t\text{-}men)_3]^{3+}$ is 450 mV more positive than $[Co(en)_3]^{3+}$, indicating the destabilizing effect that axially oriented substituents have on the Co(III) complex.

$[Co(tn)_3]^{3+}$ has a reduction potential 300 mV more positive than $[Co(en)_3]^{3+}$. The larger ring as compared to $[Co(en)_3]^{3+}$ substantially destabilizes the Co(III) relative to Co(II).

In the tris-bidentate complexes the ring-size argument holds, as can be seen from the series *mer*-$[Co(dien)_2]^{3+}$, −0.21 V; $[Co(pet)_2]^{3+}$, −0.13 V; *mer*-$[Co(dpt)_2]^{3+}$, +0.28 V. In addition, *N*-alkylation of the ligands increases the reduction potential. The group of tridentate ligands that can only coordinate facially, tap, tab, tacn, metacn, tacd, and tame, all have rather negative (more difficult to reduce) reduction potentials, −0.29 to −0.41 V. This is not necessarily a consequence of the *fac* geometry per se. It may reflect the rather rigid nature of all these ligands when coordinated, although the two *fac* isomers of $[Co(dien)_2]^{3+}$ have lower reduction potentials than the *mer* isomer, at least in acetone.

Complexes of sexadentate ligands display a wide range of reduction potentials. The lowest reduction potentials reported for any cobalt(III) hexaamine are −0.61 V for the diamcyclam complex and −0.62 V for *fac* ob_3 $[Co(diAmpnsar)]^{3+}$. Both of these complexes are expected to have unusually short Co–N bond lengths; this has been confirmed for the diamcyclam complex (*149*).

It follows, since the energy of the first spin-allowed transition (ν_1) correlates with the mean Co(III)–N bond length (*vide supra*) and ν_1 is also correlated with $E_{1/2}$ (*102*), that $E_{1/2}$ is correlated to the mean Co(III)–N bond length. This seems intuitively reasonable, since the mean Co(III)–N bond length is a rough measure of the ability of a particular ligand set to accommodate the Co(III) and Co(II) ions. The shorter the mean Co(III)–N bond length the more stable should be the smaller Co(III) ion compared to the Co(II) ion; that is, the more negative the reduction potential for that complex.

This simple concept has been taken a step further by Hambley (*182*). Using molecular mechanics, the strain energy of a series of complexes was estimated for both the Co(II) and Co(III) oxidation states. Invariably the Co(III) ion was higher in strain energy. The difference in strain energy between the two oxidation states (Δ_s) varied over a large range and was found to correlate reasonably wel with the observed reduction potentials. This can be rationalized since the reduction potential is a measure of the relative stabilities of the two oxidation states, and the difference Δ_s is actually a measure of the relative ability of that ligand set to accommodate the Co(II) or Co(III) ions. The slope of the line was 73 kJ mol^{-1} V^{-1}. This can be compared, if differences in ΔS are neglected, with the value expected from thermodynamics, which comes from the relationships

$$\Delta G^0 = -n\text{F}\Delta E^0 \tag{3}$$

where ΔG^0 is the difference in the free energy; ΔE^0 is the difference in the standard reduction potentials, here assumed to be equal to $E_{1/2}$; n is the number of electrons involved in the change; and F is Faraday's constant, 96.5 kJ Mol^{-1} V^{-1}. In this case ($n = 1$), the slope of the line should be 96.5. It was concluded that steric strain is a major contributor to the observed potentials in aqueous solution.

Geselowitz (*183*) has argued similarly, although using a far simpler force field, that the relative effect of ligand strain on the two oxidation states can be estimated and used to predict comparative reduction potentials.

Bond and Oldham (*184, 185*) have pointed out that when a variety of conformations are possible for a complex ion in either or both oxidation states the simple electrochemical model

$$A^{n+} + e^- \overset{E^0}{\rightleftharpoons} B^{(n-1)+} \tag{4}$$

cannot be correct, and account must be taken of conformational differences. For example, a model that may be applicable to some cobalt hexaamine systems is the series of reduction reactions

$$\begin{tikzcd}
A_1^{n+} + e^- \arrow[r, shift left, harpoon, "E_1^{o}"] \arrow[d, shift left, harpoon] \arrow[d, phantom, "K_1"', shift right=3] & B_1^{(n-1)+} \arrow[l, shift left, harpoon] \arrow[d, shift left, harpoon] \arrow[d, phantom, "K_2", shift left=3] \\
A_2^{n+} + e^- \arrow[r, shift left, harpoon, "E_2^{o}"] \arrow[u, shift left, harpoon] \arrow[d, shift left, harpoon] \arrow[d, phantom, "K_3"', shift right=3] & B_2^{(n-1)+} \arrow[l, shift left, harpoon] \arrow[u, shift left, harpoon] \arrow[d, shift left, harpoon] \arrow[d, phantom, "K_4", shift left=3] \\
A_3^{n+} + e^- \arrow[r, shift left, harpoon, "E_3^{o}"] \arrow[u, shift left, harpoon] & B_3^{(n-1)+} \arrow[l, shift left, harpoon] \arrow[u, shift left, harpoon]
\end{tikzcd}$$

where the K represents an equilibrium constant of some isomerization. Application of this model requires a knowledge of the distribution of these isomers in solution. Molecular mechanics calculations have been used for this purpose in the study of the electrochemical behavior of $[Co(dien)_2]^{3+/2+}$ (*97*) and $[Co(\pm-pn)_3]^{3+}$ (*39*). In the case of the *mer*-$[Co(dien)_2]^{3+/2+}$ complexes, it was concluded that the same conformation ($\delta\lambda,\delta\lambda$) (see Fig. 6) is the most stable in both oxidation states, and therefore the simple model of electron transfer should be adequate. The two other isomers, u-*fac* and s-*fac*, were predicted to have several conformations populated in both oxidation states; however, their energies are not greatly different and so although the Bond–Oldham model should hold, the E^0 values are predicted to be too similar to observe any significant differences. This investigation (*97*) did, however, predict that the E^0 values for the three isomers would be measurably different with reduction potentials, increasing in order s-*fac* > u-*fac* > *mer*, as was observed experimentally (*186*).

For $[Co(\pm\text{-}pn)_3]^{3+/2+}$ (*39*) the conformations in the (III) state are fixed by the configuration of the ligand. In the (II) state however it is likey that the isomers are able to equilibrate rapidly due to the lability of the Co(II) complexes. The *fac*/*mer* isomerization in this system appears to contribute little to the strain energy of the system and was ignored in this study. The observed reduction potentials for the four conformational isomers *lel*$_3$, *lel*$_2$*ob*, *lelob*$_2$ to *ob*$_3$ in acetone were measured and found to vary within the predicted range. Some nonreversible behavior (in the simple theory) was observed and attributed to rearrangement of the conformers in the Co(II) state.

It must be said that the Bond–Oldham model is chemically reasonable; that is, conformers can display very large differences in reduction potentials. For example, the *lel*$_3$ and *ob*$_3$ isomers of [Co(diAmpnsar)]$^{3+}$ have reduction potentials differing by 300 mV (*150*). However, in systems with rapidly interconverting conformers, the energy differences between conformers are generally rather small, which leads to the conclusion that the differences in reduction potentials will also be small, making the model difficult to test.

In addition to the structural properties, some more general parameters affect the observed reduction potential. Mayer et al. (*187, 188*) have studied the effect of the solvent on the redox potential of [Co(en)$_3$]$^{3+}$. In a range of organic solvents the polarographic reduction is reversible and the reduction potentials shift to more negative values with increasing basicity of the solvent. This is attributed to increased H-bonding between the solvent and the amine hydrogens as the solvent becomes more basic. Lay (*189*) has also discussed the effect of specific H-bonding on the thermodynamics and kinetics of electron transfer. Hydrogen bonding stabilizes the Co(III) state because of the greater polarization of the N–H bonds by the much higher charge density of Co(III) relative to Co(II). In a given solvent it seems reasonable to expect that complexes that can strongly H-bond with the solvent would be more difficult to reduce than those that cannot, all other factors being equal. Therein lies the problem—there is no system where all other factors remain equal or even relatively constant. For this reason it is difficult to ascribe any observed difference in reduction potential to a particular factor.

The presence of functional groups on the ligands can have a considerable effect on the reduction potential of a complex. Most of the ligands considered in this chapter have no functional groups other than the coordinating amines. [Co(sar)]$^{3+}$ derivatives, however, have been synthesized with a large range of substituents on the bridgehead carbon (*190*). There is a range of ~0.6 V for this series of substituted complexes. The steric requirements of the ligands are relatively constant, and the observed range represents mainly the inductive effect of the substituents. The comparison of the potentials of [Co(sar)]$^{3+}$, [Co(diClsar)]$^{3+}$, and [Co(diNOsar)]$^{3+}$ (-0.40, -0.14, and $+0.04$ V, respectively), shows the inductive effects of two electron-withdrawing groups.

VI. Electron Self-Exchange Reactions

A. BACKGROUND

Since the beginnings of experimental and theoretical investigations of electron-transfer reactions, the various cobalt amine complexes have always been, and still are, important case studies (*191*). The situation for $[CoN_6]^{3+/2+}$ self-exchange reaction systems is quite complex, owing to the combination of the electron-transfer process with the rearrangement of the electronic structure. The reduction of a low-spin $t_{2g}{}^6$ Co(III) amine complex invariably produces a high-spin Co(II) species with a $t_{2g}{}^5\ e_g{}^2$ electronic configuration. Accordingly, the assessment of the various contributions determining electron-transfer rates (*vide infra*) is quite complicated and some ambiguities have been resolved only recently (*192, 193*). This section deals with the outer-sphere reaction.

$$\begin{aligned} &[CoN_6]^{3+} + [Co^*N_6]^{2+} \xrightarrow{k_{obs}} [CoN_6]^{2+} + [Co^*N_6]^{3+} \\ &{}^1A_{1g}\,(t_{2g}^6) + {}^4T_{1g}\,(t_{2g}^5e_g^2) \longrightarrow 4T_{1g}\,(t_{2g}^5e_g^2) + 1A_{1g}\,(t_{2g}^6) \end{aligned} \tag{6}$$

Since both reactants, the Co(III) and the Co(II) complex, have the same donor set of ligands, we are dealing with the paradigmic case of a reaction without a chemical change. Experimental studies of such self-exchange reactions must employ suitable isotopic labels at the metal center (*194*) or within the the ligand molecule (*193*), or must monitor the reduction process with a chiroptical technique (*166*).

Marcus theory provides the appropriate formalism to rationalize the wide range of electron-transfer rate observed for the self-exchange reactions of inorganic as well as organic redox couples. The different factors contributing to the activation barrier of the fundamental redox process and corresponding model calculations were thoroughly discussed in three comprehensive reviews (*195–197*). Generally, the rate of a self-exchange reaction is expressed in transition-state theory as the product of the equilibrium constant K for the formation of the precursor complex and the electron-transfer rate within this pre-formed association complex.

$$[CoN_6]^{3+} + [Co^*N_6]^{2+} \overset{K}{\rightleftharpoons} \{CoN_6^{3+}\text{–}Co^*N_6^{2+}\} \xrightarrow{k_{et}} \{CoN_6^{2+}\text{–}Co^*N_6^{2+}\} \tag{7}$$

where k_{obs} equals $K \cdot k_{et}$. The equilibrium constant K is calculated considering the diffusion process (collision frequency, Z) and the coulombic energy required to form the association complex dimer from two infinitely separated positive ions (work term, w_d) (*195–197*).

The two coordination geometries, in particular the metal-ligand distances, of the two reactants within the precursor complex are different. In other words, the precursor consists of genuine Co(III) and Co(II) species, with short and long Co–N bond lengths, respectively, and corresponding force constants for the vibrational modes. Microscopic reversibility requires the formation of an activated transition state with coordination shells of equal energy. Thermally activated vibrational fluctuations create a situation where the two coordination environments become energetically indistinguishable; that is, the precursor becomes an electronicaly degenerate activated state. Electron transfer occurs within this transition-state dimer, and the two complex ions vibrationally relax to their respective equilibrium geometries. Finally, this successor complex dissociates into products, which may or may not undergo further reactions, (e.g., ligand substitution for the labile Co(II) species). In this general framework, Marcus theory formulates the electron-transfer rate as a product of three factors:

$$k_{\text{et}} = \kappa_{\text{el}} \bullet \kappa_{\text{n}} \bullet \nu_{\text{n}} \tag{8}$$

where κ_{el} = electronic factor; κ_{n} = nuclear factor; ν_{n} = effective nuclear frequency.

The electronic factor κ_{el} is a function of the electronic interaction between the reduced (A) and oxidized (B) metal center, expressed as the electronic coupling matrix element H_{AB}. H_{AB} can be calculated from first principles (*195–197*) or can be estimated from the intensity of the intervalence band of chemically closely related mixed-valence dimers (*198*). When H_{AB} is large, κ_{el} is equal to 1 and the reaction is said to be adiabatic.

Within the classical limit the nuclear factor is given by the rate expression

$$\kappa_{\text{n}} = \exp(-\Delta G^{*}/RT) \tag{9}$$

The free energy of activation ΔG^{*} consists of two parts, $\Delta G^{*}{}_{\text{in}}$ and $\Delta G^{*}{}_{\text{out}}$. The first contribution, $\Delta G^{*}{}_{\text{in}}$, represents the energy investment to adapt the two coordination environments within the precursor to the degenerate transition state geometry. This energy of the concerted contraction and expansion of the two coordination shells is given by

$$\Delta G^{*}_{\text{in}} = \frac{1}{8} \sum f_i \, (d_2^0 - d_3^0)\, i^2 \tag{10}$$

where $f_i = 2f_2f_3/(f_2 + f_3)$, the reduced force constant for the *i*th inner sphere vibration; $d_2{}^0 - d_3{}^0$ is the corresponding equilibrium bond distance in the two oxidation states; and the sum is over all intramolecular vibrations (*195–197, 199*).

The second contribution, ΔG^*_{out}, is the energy involved in reorganization of the solvent shell prior to electron transfer. This part of the activation energy is calculated by treating the solvent as a dielectric continuum with refractive index n and a static dielectric constant D_s. Moreover, the two reactants are commonly approximated by spheres of radii a_2 and a_3. If the distance r between the centers of the two redox partners in the activated complex is assumed to be equal to the sum of a_2 and a_3, then,

$$\Delta G^*_{\text{out}} = e^2 \cdot \frac{1}{4}\left(\frac{1}{2}a_2 + \frac{1}{2}a_3 - \frac{1}{r}\right)\left(\frac{1}{n^2} - \frac{1}{D_s}\right) \tag{11}$$

The effective nuclear frequency ν_n, finally, depends on ΔG^*_{out} and ΔG^*_{in} and on two frequencies ν_{in} and ν_{out}. ν_{in} is the frequency of the metal-ligand stretching mode, whereas ν_{out} corresponds to the frequency of reorientation of the solvent dipoles. Numerically, ν_{in} is of the order of 400 cm^{-1} and ν_{out} for aqueous solutions is about 30 cm^{-1}.

It has to be emphasized that all the various contributions to K and k_{et} depend very strongly on r, the distance separating the metal centers in the two oxidation states within the transition-state complex. Van der Waals contact or even an interpenetration of the coordination shells are the limiting situations. Model calculations must explicitly consider the relative orientations of the two reacting octahedra (psuedo-octahedra) in the formation of the encounter dimer. The docking geometry, for example, whether the two octahedra meet each other face to face or apex to face, determines the crucial parameter r. For optically active complexes this distance obviously depends on the combination of the reacting isomers. Recent work dealing with the stereospecificity of electron transfer reactions is beginning to yield some information on the docking geometries *(200, 201)* (*vide infra*).

Classical, semi-classical, and quantum mechanical procedures have been developed to rationalize and predict the rates of electron transfer. In summary, the observed rate of a self-exchange reaction can be calculated as a function of interatomic distances, force constants, electronic coupling matrix element, and solvent parameters. These model parameters are either calculated, estimated, or determined by experiment, in each case with a corresponding standard deviation. Error propagation immediately demonstrates that calculated rates have error ranges of roughly two orders of magnitude, independent of the level of sophistication in the numerical procedures.

For electron-transfer reactions with a net driving force such as

$$[\text{CoN}_6]^{3+} + \text{Red} \overset{k_{12}}{\rightleftharpoons} [\text{CoN}_6]^{2+} + \text{Ox} \tag{12}$$

the rate k_{12} can be expressed as a functin of k_{11} and k_{22}, the two self-exchange rates for the $[CoN_6]^{3+/2+}$ and the Ox/Red couple, respectively, and the driving force for the reaction. The Marcus cross relation has the form (*202*)

$$k_{12} = [k_{11} \cdot k_{22} \cdot K_{12} \cdot f_{12}]^{1/2}$$

and

$$\log(f) = (\log K_{12})^2/4 \log(k_{11} \cdot k_{22}/Z^2) \qquad (13)$$

where K_{12} is the equilibrium constant for the reaction and Z is the collision frequency. It has been shown that this equation interconnects k_{11}, k_{22}, and k_{12} provided that the driving force for the reaction is moderate to small.

For reactions with a small driving force the Marcus cross relationship usually gives consistent results, within two orders of magnitude at least (*192, 203–205*). A major difficulty with applying this method more generally is that for many common reducing agents the self-exchange rate constants are not known accurately, even within an order of magnitude.

B. OBSERVATIONS

The reduction of $[Co(en)_3]^{3+}$ and $[Co(NH_3)_6]^{3+}$ by V^{2+} (*206, 207, 208, 209, 210*), Cr^{2+} (*207, 208*), Eu^{2+} (*207, 211*), $[Cr(bipy)_3]^{2+}$ (*207, 209*), $[Ru(NH_3)_6]^{2+}$ (*211*), Yb^{2+} (*213*), U^{3+} (*214, 215*), and $[Ru(NH_3)_5Cl]^{+}$ (*209*) has been studied; the results have been reviewed by Geselowitz and Taube (*204*). The predicted self-exchange rates obtained by application of the cross relationship for the $[Co(en)_3]^{3+/2+}$ couple are mostly within an order of magnitude of the directly measured value (*204, 194, 166*).

A problem with the measurement of the self-exchange rate for the $[Co(NH_3)_6]^{3+/2+}$ couple is that even in 6 M aqueous NH_3, there is a significant proportion of the Co(II) present in the form of $[Co(NH_3)_5OH_2]^{2+}$ (*204*). Also, hydrolysis of $[Co(NH_3)_6]^{3+}$ in the basic media at high temperatures can lead to serious error. A recent measurement of the self-exchange rate for the hexaammine couple (*195*) found the measured value was much higher than had been previously estimated (*216*) and in the region of that predicted by application of the Marcus cross-relationship. There is now no large discrepancy between the calculated and observed rates of self-exchange for the $[Co(NH_3)_6]^{3+/2+}$ couple.

For homoleptic cobalt(III/II) amines, a relatively large number of self-exchange rates have been directly determined; the rate constants span six orders of magnitude. The rates of the self-exchange reactions for many other complexes have been estimated by application of the Marcus cross relationship. The data that are available are shown in Table IV.

TABLE IV

SELF-EXCHANGE RATE CONSTANTS

Couple	k_{11}[a] $M^{-1}s^{-1}$	Method[b]	Reference
$[Co(NH_3)_6]^{3+/2+}$	$(8 \pm 1) \times 10^{-6}$ [c]	A	*(193)*
	$(3.9 \pm 1.5) \times 10^{-6}$ [d]	A	*(193)*
$[Co(en)_3]^{3+/2+}$	5.2×10^{-5}	A	*(194)*
	7.7×10^{-5}	A	*(166)*
$[Co(chxn)_3]^{3+/2+}$	$\sim 10^{-4}$ [e]	B	*(209)*
$[Co(tmen)_3]^{3+/2+}$	9×10^{-8}	B	*(162)*
$[Co(metacn)_2]^{3+/2+}$	0.19[f]	A	*(120)*
$[Co(dien)_2]^{3+/2+}$	1.9×10^{-4}	B	*(102)*
$[Co(medien)_2]^{3+/2+}$	8×10^{-4}	B	*(102)*
$[Co(etdien)_2]^{3+/2+}$	5.9×10^{-4}	B	*(102)*
$[Co(budien)_2]^{3+/2+}$	6.4×10^{-5}	B	*(102)*
$[Co(pet)_2]^{3+/2+}$	3.6×10^{-4}	B	*(102)*
$[Co(linpen)]^{3+/2+}$	6.0×10^{-4}	B	*(102)*
$[Co(dtne)]^{3+/2+}$	1.3×10^{-3}	B	*(102)*
$[Co(taptacn)]^{3+/2+}$	$(4.2 \pm 0.5) \times 10^{-2}$ [g]	A,B	*(129)*
$[Co(sep)]^{3+/2+}$	5.1 ± 0.3 [h]	A	(6)
$[Co(sar)]^{3+/2+}$	2.1 ± 0.2 [i]	A	*(218)*
$[Co(diAmsar)]^{3+/2+}$	0.5[i]	A	*(218)*
$[Co(dAmsarH_2)]^{5+/4+}$	0.024[i]	A	*(218)*
$[Co(diAmpnsarH_2)]^{5+/4+}$ (*lel*$_3$)	0.031[i]	A	*(150)*
$[Co(diAmpnsarH_2)]^{5+/4+}$ (*ob*$_3$)	0.98[i]	A	*(150)*
$[Co(diAmchxnsar)]^{3+/2+}$	1.1 ± 0.2 [i]	A	*(220)*
$[Co(diAmchxnsar)]^{5+/4+}$	0.038[h]	A	*(220)*
$[Co(amsartacn)]^{3+/2+}$	$(8.6 \pm 0.6) \times 10^{-2}$ [h]	A	*(218)*
$[Co(amsartacn)]^{4+/3+}$	$(4.0 \pm 0.4) \times 10^{-2}$ [h]	A	*(218)*

[a] In water at 25°C, 1 M ionic strength.

[b] A, direct measurement of the exchange reaction; B, estimate of the self-exchange rate by application of the Marcus relationship to cross reactions.

[c] 40°C, $\mu = 2.5$ M ($CF_3SO_3^-$ medium).

[d] 40°C, $\mu = 2.5$ M (Cl^- medium).

[e] By comparison with $[Co(en)_3]^{3+/2+}$ after measurement of a number of cross reactions.

[f] $\mu = 0.1$, measured as the rate of exchange between $[Co(R\text{-}metacn)]^{3+}$ and $[Co(S\text{-}metacn)]^{2+}$.

[g] $\mu = 0.1$ M.

[h] Very large driving force.

[i] $\mu = 0.2$ M.

We have noticed a correlation between the logarithm of the self-exchange rate constant for a series of $[\mathrm{CoN_6}]^{3+/2+}$ couples and the degree of substitution at the coordinated amines as judged by the number of amine protons in the complex (Fig. 12). It should be noted that more than half the points that fall on the line have been estimated by application of the cross relationship to the rate of a single cross reaction with V^{2+} (*102*). Not all the points in the plot are homoleptic complexes; some mixed ligand $\mathrm{CoN_6}$ complexes were included because of the need to try to verify the unexpected observation. The line in Fig. 12 was

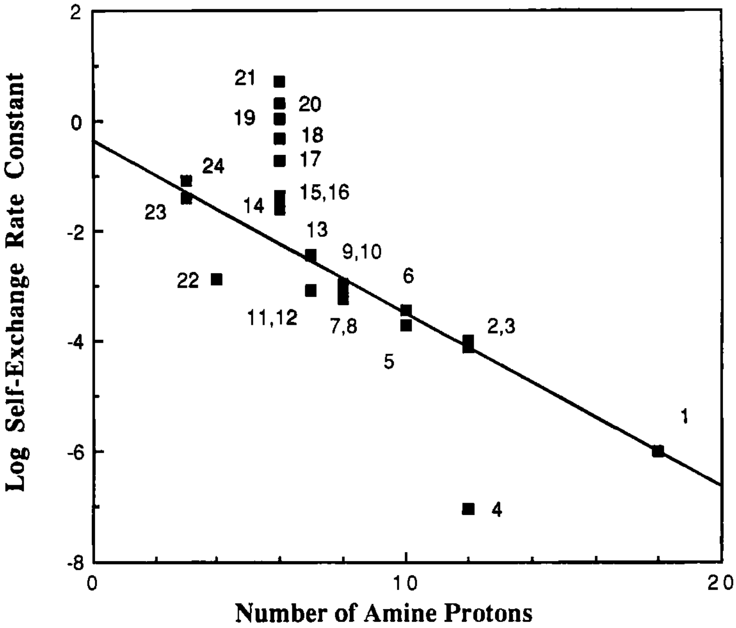


FIG. 12. Plot of number of amine protons versus log of the self-exchange rate constant ($\mathrm{M^{-1}s^{-1}}$) for cobalt hexaamine complexes at 25°C. No correction has been made for ionic strength differences. The data include some nonhomoleptic complexes. (1) $[\mathrm{Co(NH_3)_6}]^{3+/2+}$, (2) $[\mathrm{Co(en)^3}]^{3+/2+}$, (3) $[\mathrm{Co(chxn)^3}]^{3+/2+}$, (4) $[\mathrm{Co(tmen)^3}]^{3+/2+}$, (5) $[\mathrm{Co(dien)^2}]^{3+/2+}$, (6) $[\mathrm{Co(pet)^3}]^{3+/2+}$, (7) $[\mathrm{Co(linpen)}]^{3+/2+}$, (8) $[\mathrm{Co(medien)}]^{3+/2+}$, (9) $[\mathrm{Co(tacn)(dien)}]^{3+/2+}$, (10) $[\mathrm{Co(tacn)(pet)}]^{3+/2+}$, (11) $[\mathrm{Co(tacn)(etdien)}]^{3+/2+}$, (12) $[\mathrm{Co(tacn)(budien)}]^{3+/2+}$, (13) $[\mathrm{Co(tacn)(medien)}]^{3+/2+}$, (14) $[\mathrm{Co(diAmsar)}]^{5+/4+}$, (15) $[\mathrm{Co(taptacn)}]^{3+/2+}$, (16) $[\mathrm{Co(metacn)^2}]^{3+/2+}$, (17) $[\mathrm{Co(diAmsar)}]^{3+/2+}$, (18) $[\mathrm{Co(sar)}]^{3+/2+}$, (19) $[\mathrm{Co(sep)}]^{3+/2+}$, (20) $[\mathrm{Co(dtne)}]^{3+/2+}$, (21) $[\mathrm{Co(Amsartacn)}]^{4+/3+}$, (22) $[\mathrm{Co(Amsartacn)}]^{3+/2+}$, (23) $[\mathrm{Co(diAmchxnsar)}]^{3+/2+}$, (24) $[\mathrm{Co(diAmchxnsar)}]^{5+/4+}$. The data for homoleptic complexes are taken from Table IV; the other data are from reference (*102*). The line was calculated without the data for the sep and sar derivative cages and the $[\mathrm{Co(tmen)_3}]^{3+/2+}$ couple.

calculated (linear least squares) ignoring the data for the capped tris-bidentate cages (sep, sar, and derivatives) and the datum point for the $[Co(tmen)_3]^{3+/2+}$ reaction, points 4, 14, 15, 18, 19, 20, 21. If this relationship is substantiated by accurate measurement or estimation of further reactions it may indicate a direction for research into the question of rates of electron-exchange reactivity. The physical basis for this relationship is currently not understood. The possibilities will be discussed following some more specific observations on comparison of electron-exchange reactivity (vide infra).

Beattie et al. (*209*) have estimated that the rate of self-exchange for the $[Co(chxn)_3]^{3+/2+}$ couple is approximately the same as for $[Co(en)_3]^{3+/2+}$. This assertion was made after the measurement of the rate of the reduction of $[Co(en)_3]^{3+/2+}$ and $[Co(chxn)_3]^{3+/2+}$ (mixture of isomers) by three reducing agents. The reduction potentials of the two complexes differ only slightly, and because the two complexes were reduced at about the same rates and with similar activation parameters, the self-exchange rate constants should be similar. The implication (because the chxn complex has sterically hindered C_2 faces) in these results is that either the self-exchange reactions for both couples proceed through an activated complex in which the reactants are aligned along their respective C_3 axes, or the precursor complex involves an interaction of the complexes, including the C_2 face of the complexes, and the probability of electron transfer through the chxn ring is the same as through the en ring. The former argument appears to be more probable.

In contrast to this result, it has been inferred from the results of several cross-reactions that the self-exchange rate for the $[Co(tmen)_3]^{3+/2+}$ couple (*162*), which like $[Co(chxn)_3]^{3+/2+}$ has sterically hindered C_2 faces, is approximately three orders of magnitude less than for $[Co(en)_3]^{3+/2+}$.

The blocking of the C_3 faces of $[Co(en)_3]^{3+/2+}$ as occurs in $[Co(sep)]^{3+/2+}$ and sar couples, results in an increase of five orders of magnitude in the self-exchange rate constant over $[Co(en)_3]^{3+/2+}$ (*6, 7*). This indicates that many factors apart from access to a particular face and steric factors are involved in the electron-exchange reactions. The question arises then: Why should these cages, which are not greatly different from $[Co(en)_3]^{3+/2+}$ in electronic structure and Co–N bond lengths, differ so greatly in the rate of electron self-exchange?

Endicott et al. (*217*) have suggested that a large proportion of the difference in the activation energies between the $[Co(en)_3]^{3+/2+}$ and the $[Cosep]^{3+/2+}$ reactions (87 versus 58 kJ mol^{-1}) lies in the reported differences in Δd for the two couples, 0.21 Å and 0.17 Å respectively.

Since the publication of this report another structural determination of $[Co(sep)]^{3+}$ has been completed (*152*). The mean Co–N bond length, 1.974 Å, gives a Δr value for the reaction of 0.19 Å and considerably reduces the significance of this argument.

One possibility for the fast self-exchange reaction of the $[Co(sep)]^{3+/2+}$ couple was that the ions were able to communicate through the lone pair of electrons on the bridgehead nitrogens (*218*). The similarly rapid rates observed for the $[Co(sar)]^{3+/2+}$ and derivatives shows that this path is not important. Another prospect was that the considerably larger caged ions benefit from reduced solvation and hence solvent reorganization energies. This however seems not to be the case in the reactions of $[Co(chxn)_3]^{3+/2+}$ (*209*) and $[Co(tmen)_3]^{3+/2+}$ (*162*).

Geselowitz (*183*) has suggested that a significant part of the difference in the activation energy between the $[Co(en)_3]^{3+/2+}$ and $[Co(sep)]^{3+/2+}$ reactions arises from the strain inherent in the sep ligand making the transition state more accessible. The ΔG_{in} (inner sphere reorganization energy) was calculated to be reduced by 10 kJ mol^{-1} compared to the $[Co(en)_3]^{3+/2+}$ case. In essence this treatment reduces the value of the effective Co–N deformation force constants. This is in contrast to the estimate by Endicott et al. (*217*) that the force constant for the two systems in the Co(III) state differ by less than 10%.

Geue et al. (*219*) have considered strain imposed on the metal ions in both oxidation states by the cage ligand. Using molecular mechanics it is estimated that the ligand cavity size, although varying with the conformation of the complex, is intermediate between Co(II) and Co(III). The observed increase in rate of electron transfer for the cage systems is due largely to the ligand effectively destabilizing the ground state(s) for the reaction relative to the transition state.

Interestingly the caged complex derived from $[Co(chxn)_3]^{3+}$ undergoes the electron self-exchange reaction at a very similar rate to that of the unsubstituted cage (*220*). This is despite the larger size of the chxn cage. This is difficult to rationalize unless the increase in k_{et} achieved by reducing r, the separation between the ions, is almost completely offset by the decrease in K due to the repulsion between the similarly charged ions; that is, the quantity, $k_{obs} = k_{et} \cdot K$, is relatively constant over the range of r values applicable to these two reactions. This naive argument however implies that, at least at the larger values of r, the electron transfer is nonadiabatic. If both the reactions are adiabatic, as is generally assumed, then more specific effects (such as the strain arguments *vide supra*) are required to explain the coincidence of rate constants.

Returning to the correlation we have observed between the rate constant for the self-exchange reaction and the degree of alkylation of the amine ligands. As the number of amine protons decreases, the average size of the complexes increases. This may account for some of the difference as the work required to bring the two positively charged reactants together decreases with increasing size. This cannot account for a 10^5 increase in rate between $[Co(NH_3)_6]^{3+/2+}$ and the tacnsar cages, however. Another possible factor is the hydrophilicity of the complexes. As the complexes become more alkylated they become more hydrophobic, and this may increase the equilibrium constant for the precursor complex by introducing hydrophobic interactions between the reactants in addition to reducing the solvation of the complexes. A third possible explanation may relate to the steric effect as discussed by Geselowitz (*183*) and Geue et al. (*219*); the more highly substituted amine complexes are accelerated in the self-exchange reactions by the steric demands of the ligands. The more substituted amines may prefer a coordination geometry intermediate between that provided by Co(II) and Co(III), thereby stabilizing the transition state for the reaction. The deviation of the "cages" from the line of correlation may be due to their more rigid nature being more effective at deforming the coordination sphere.

Chiral discrimination can occur in either or both steps of the electron-transfer process:

$$\text{Ox} + \text{Red}^* \rightleftharpoons \{\text{Ox..Red}^*\} \qquad K \tag{14}$$

$$\{\text{Ox..Red}^*\} \rightleftharpoons \text{Red} + \text{Ox}^* \qquad k_{et} \tag{15}$$

Geselowitz et al. (*200*) showed that the oxidation of $\Lambda,\Delta\text{-}[Co(en)_3]^{2+}$ by $\Delta[Co(edta)]^-$ results in the production of $\Lambda[Co(en)_3]^{3+}$ in excess of the other enantiomer, and vice versa for $\Lambda[Co(edta)]^-$. The enantiomeric excess was around 9% in H_2O but rose with decreasing solvent polarity to 40% in sulfolane. The substitution of the "en" backbone of edta with alkyl groups has a negligible effect on the enantiomeric excess of $[Co(en)_3]^{3+}$ or on the rate of the reaction. This seems to be evidence for the view that the selectivity arises from the pre-equilibrium step of the reaction and that $[Co(edta)]^-$ and analogues were oriented with a carboxylate face toward the $[Co(en)_3]^{2+}$ ion. The same conclusion was reached (*221*) in the study of the ion pair formation between $[Co(edta)]^-$ and $[Co(en)_3]^{3+}$; that is, that the stronger ion pairs were formed between complexes of opposite absolute configuration and that $[Co(edta)]^-$ associated via its pseudo-C_3 carboxylate face.

Essentially the same conclusion is drawn after a study of the [Co-

$(edta)]^-$ oxidation of a series of substituted $[Co(en)_3]^{2+}$ complexes which, because of the substituents on the "en" rings, are resolvable into conformational isomers (*201, 222*). It was also shown that for the oxidation of $[Co(en)_3]^{2+}$ (by comparison of the stereoselectivity observed in the presence and absence of PO_4^{3-}), $[Co(\pm\text{-}2,3\text{-}bn)_3]^{2+}$ and $[Co(\pm\text{-}chxn)_3]^{2+}$ by $\Delta[Co(edta)]^-$, the Δ-Λ stereoselectivity increased with the number of rings in the *ob* conformation (*222*), corresponding to a change in approach from the C_3 to the C_2 axis of the tris-diamine complex. In energy terms, the stereoselectivity is very modest, amounting to a difference in activation energy of 1.2 kJ mol^{-1} in the most extreme case, 25% stereoselectivity. These authors have speculated that the difference in the rates of the two reactions may be due to a difference in the separation distance *r* between the two reactants and, using the equations given above, have estimated that to observe a difference in rate of 10% between two enantiomers a difference in *r* of only 0.03 Å is required.

A difference in the rate constants was observed for the reduction of $(-)[Co(diAmsarH_2)]^{5+}$ with $(+)$ and $(-)[Co(sep)]^{2+}$. The enantiomer $(-)[Co(sep)]^{2+}$ reduces the protonated diAmsar cage complex with a rate constant that is 10% greater than for its enantiomer (*218*). This is of the order of selectivity observed in the oxidation of $[Co(en)_3]^{2+}$ by $[Co(edta)]^-$ in aqueous conditions, and it is apparent that the effect is not dependent on the complexes being oppositely charged (i.e., the ability to form stable ion pairs).

These stereoselectivity experiments appear to indicate that the reactants approach each other quite closely during the electron-transfer process. It should be possible by judicious choice of reactants to increase substantially the stereoselectivity observed in the above systems. This may in the future make a significant contribution to our understanding of the mechanisms of electron transfer reactions both in chemical systems and in biology, where electron-transfer reactions occur in a very asymmetric environment.

VII. Concluding Remarks

LEWIS BASICITY OF THE AMINES

This chapter has been concerned with the effect of structural properties of cobalt(III) hexaamines on their other properties. Included in this review have been complexes ranging from cobalt hexaammine, to complexes composed of three secondary and three tertiary amine donors (the Amsartacn cages). It is known that in the gas phase the degree of alkylation of an amine has a significant effect on its basicity. Munson (*223*) has shown that in the gas phase the proton affinity of amines, in particular increasing methyl substitution of ammonia, increased with increasing substitution. Coordination of amines to gas-phase metals has also shown that the M–L bond enthalpy increases in the order $NH_3 < NH_2Me < NHMe_2 < NMe_3$ for the metal ions Li^+ (*224*), Ni^+ (*225*), and $FeBr^+$ (*226*). Hancock et al. (*227*) have suggested that for Ni^{2+} amine complexes in solution secondary amines form intrinsically stronger bonds than primary amines after allowance for steric effects.

We have discussed the effects of structure on the other properties of the amine complexes predominantly in terms of steric effects. This has involved an underlying assumption that the series of amines from NH_3 to NR_3 have similar electronic properties; that is, their electron donation capability is not affected by the degree of substitution. Judging by the gas-phase results this assumption may not be justified. The UV/vis spectra in solution and the solid state crystal structures, however, do not display any trends that could be interpreted as a variation of Lewis basicity with degree of substitution. Comparison of the spectra and mean Co–N bond lengths of $[Co(NH_3)_6]^{3+}$ with $[Co(NH_2Me)_6]^{3+}$ demonstrates that if the Lewis basicity does increase with degree of substitution of the amine then, at least in this case, the steric effect of the methyl far outweighs its electronic effect. We have not found it necessary to invoke any electronic differences between the varying degrees of substitution of the amines.

VIII. Abbreviations

ama, 3-(aminomethyl)-3-methylazetidine
1,3-bn, 1,3-diaminobutane
1,4-bn, 1,4-diaminobutane
2,3-bn, 2,3-diaminobutane
budien, 1-amino-3-(2-aminoethyl)-3-azaheptane
captame, 9,17-dimethyl-13-nitro-1,3,5,7,11,15-hexaazatetracyclo-$[11.5.1.1.^{3,9}.1^{5,1}]$henicosane
chxn, 1,2-diaminocyclohexane
chxnsar, sar type cage derived from $[Co(chxn)_3]^{3+}$
chxtn, 2-aminomethylcyclohexylamine
cptn, 1-2-diaminocyclopentane
dap, 2,3-diaminopropanol
diamcyclam, 1,8-diamino-1,8-dimethyl-3,6,10,13-tetraazacyclotetradecane
diammecyclam, 1,8-diamino-1,8-diaminomethyl-4,12-dimethyl-3,6,10,13-tetraazacyclotetradecane

diAmsar, 1,8-diamino-sar
diClsar, 1,8-dichloro-sar
diNOsar, 1,8-dinitro-sar
dien, 3-aza-1,5-diaminopentane
dmbn, 3,3-dimethyl-1,2-diaminobutane
dpen, 1,2-diphenyl-1,2-diaminoethane
dppn, 1,3-diphenyl-1,3-diaminopropane
dpt, 4-aza-1,7-diaminoheptane
dtah, 1,16-diamino-3,7,10,13-tetraazahexadecane
dtne, 1,2-bis-(1,4,7-triaaza-1-cyclononyl)ethane
en, 1,2-diaminoethane
etdien, 1,5-diamino-3-ethyl-3-azapentane
ibn, 2-methyl-1,2-diaminopropane
linpen, 1,14-diamino-3,6,9,12-tetraazatetradecane
meamcha, 1-aminomethyl-2-methylcyclohexylamine
medien, 1,5-diamino-3-methyl-3-azapentane
metacn, 2-methyl-1,4,7-triazacyclononane
metach, 1-methyl-2,4,6-triaminocyclohexane
metn, 2-methyl-1,3-diaminopropane
meen, 4-amino-2-aza-butane
N, any amine, monodentate, 1/2 bidentate, 1/3 tridentate etc.
18-N-6, 1,4,7,10,13,16-hexaazacyclooctadecane
20-N-6, 1,4,7,11,14,17-hexaazacycloeicosane
21-N-6, 1,4,8,11,15,18-hexaazacycloheneicosane
NOsartacn, 9-nitro-1,4,7,11,14,19-hexaazatricyclo[7.7.4.$2^{4,14}$]docosane
pen, 1-phenyl-1,2-diaminoethane
pet, 3-aza-1,6-diaminohexane
phtn, 1-phenyl-1,3-diaminopropane
pn, 1,2-diaminopropane
pnsar, sar type cage derived from $[\mathrm{Co(pn)_3}]^{3+}$
ptn, 2,4-diaminopentane
sar, sarcophagine, 3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane
sen, 1,1,1-tris(4-amino-2-azabutyl)ethane
sep, sepulchrate, 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane
stn, 1,1,1-tris(5-amino-2-azapentyl)ethane
tab, 1,2,4-triaminobutane
tacn, 1,4,7-triazacyclononane
tacd, 1,4,7-triazacyclodecane
tach, 1,3,5-triaminocyclohexane
tae-en, *N,N,N′,N′*-tetrakis(2-aminoethyl)-1,2-diaminoethane
tae-pn, *N,N,N′,N′*-tetrakis(2-aminoethyl)-1,2-diaminopropane
tae-ptn, *N,N,N′,N′*-tetrakis (2-aminoethyl)-2,4-diaminopentane
taetacn, 1,4,7-tris(2-aminoethyl)-1,4,7-triazacyclononane
tae-tn, *N,N,N′,N′*-tetrakis(2-aminoethyl)-1,3-diaminopropane
tame, 1,1,1-tri(2-aminoethyl)ethane
tamp, 1,2,3-triamino-2-methylpropane
tap, 1,2,3-triaminopropane
taptacn, 1,4,7-tris(3-aminopropyl)-1,4,7-triazacyclononane
tmen, 2,3-dimethyl-2,3-diaminobutane
tn, 1,3-diaminopropane

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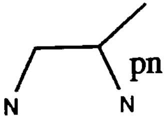
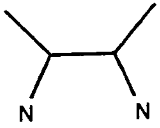
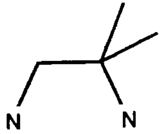
IX. Appendix

This section shows the structures of various compounds discussed in this chapter.


en


pn


2,3-bn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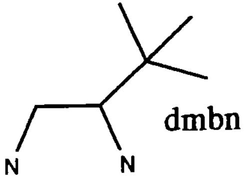
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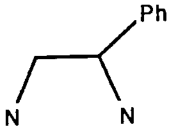
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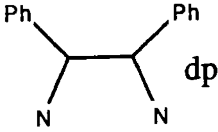
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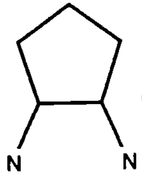
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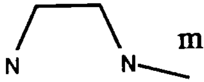
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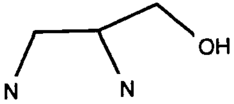
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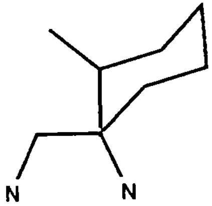
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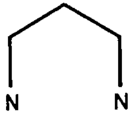
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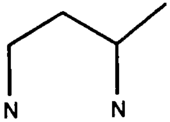
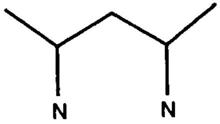

1,3-bn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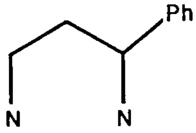
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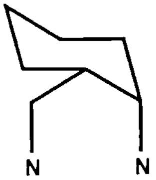

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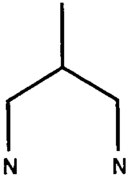

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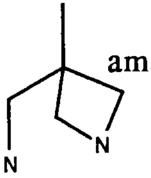

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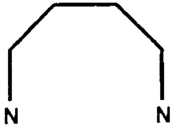

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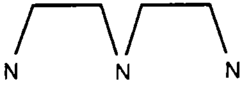

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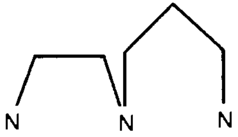

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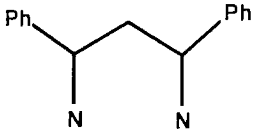

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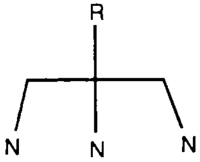
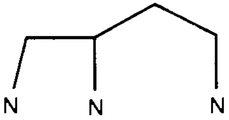


R = H: tap
R = Me: tamp



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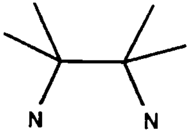
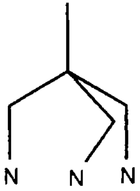
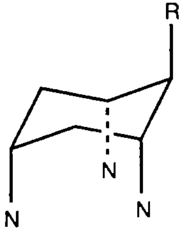


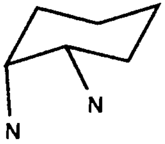
tmen



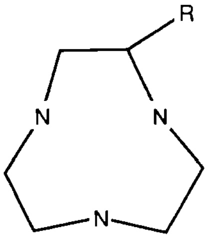
tame



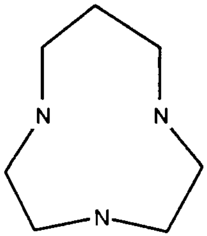
R = H: tach
R = Me: metach



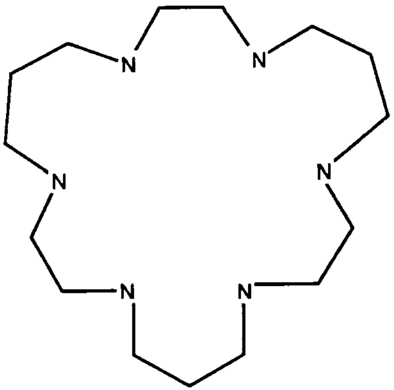
chxn



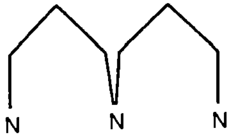
R = H: tacn
R = Me: metacn



tacd



21N6



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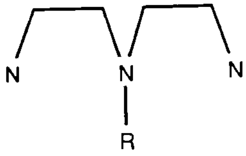
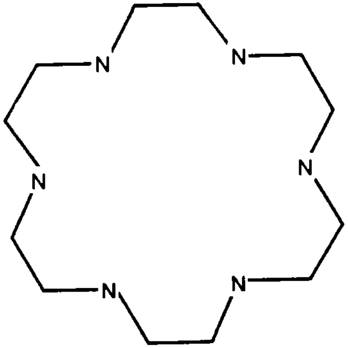


R = Me: medien
R = Et : etdien
R = Bu: budien



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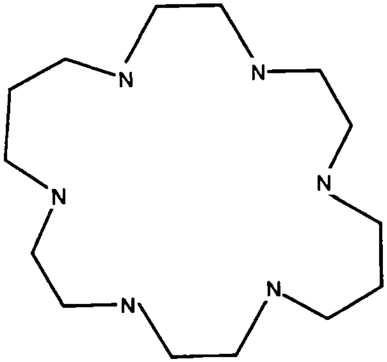

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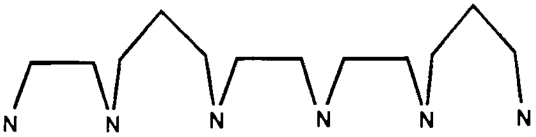
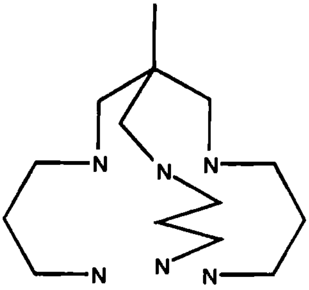
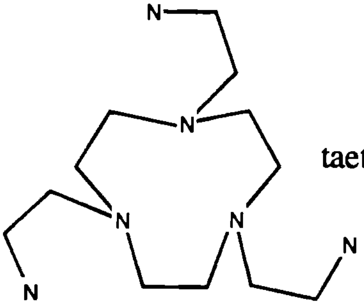


dtah

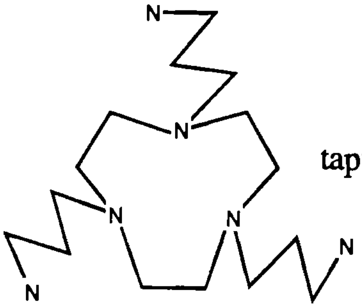
linpen



stn



taetacn



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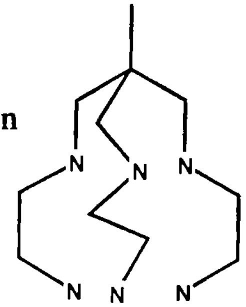
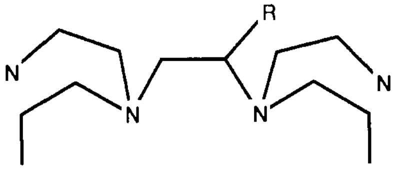
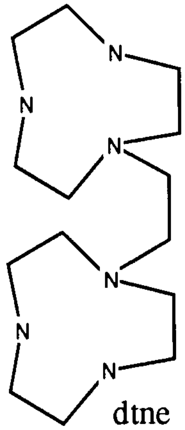


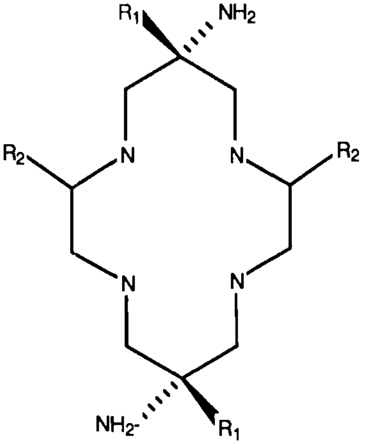
sen



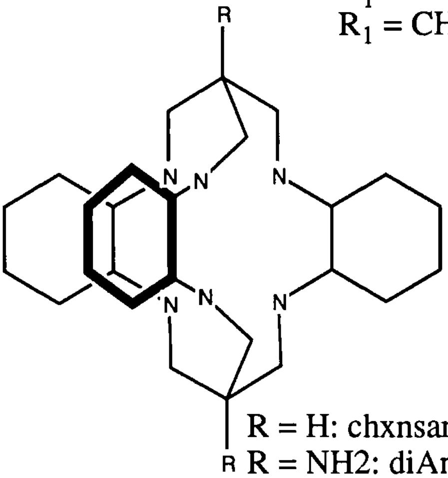
R = H: tae-en
R = Me: tae-pn



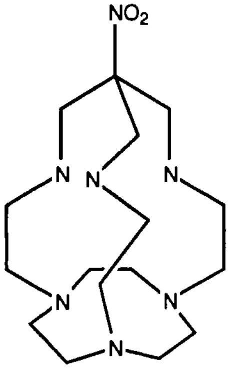
dtne



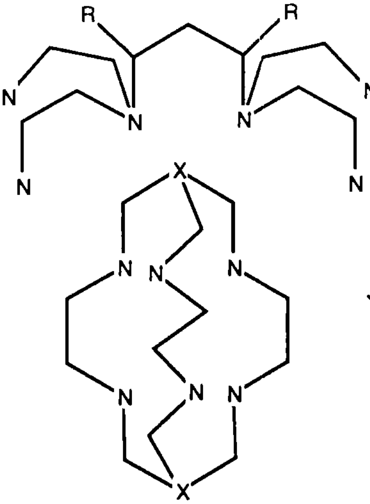
R_1 = Me, R_2 = H: diamcyclam
R_1 = CH_2NH_2 , R_2 = Me: diammecyclam



R = H: chxnsar
R = NH2: diAmchxnsar

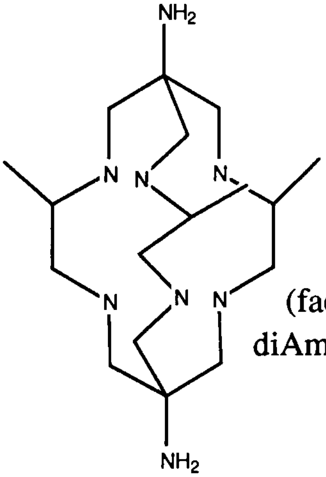


NOsartacn

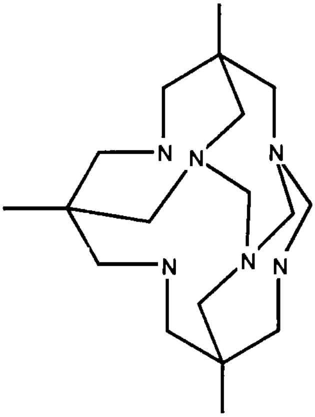


R = H: tae-tn
R = Me: tae-ptn

X = N sep
X = C-H sar



(fac)-diAmpnsar



captame

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