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MOLECULAR MECHANICS CALCULATIONS IN COORDINATION CHEMISTRY

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A. INTRODUCTION

(i) Scope and limitations of this review

We believe that molecular mechanics, frequently called conformational analysis, can provide a precise quantitative estimate of intramolecular steric effects. This review has been designed to provide a coordination chemist with an overview of molecular mechanics applications in coordination chem-

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istry. Accordingly, in Part A, only a cursory introduction to molecular mechanics has been provided (though we believe that we have given sufficient bibliographic information to satisfy a reader inclined to investigate the methodology in detail). No effort has been made to analyze the many applications of molecular mechanics to organic and biochemistry; applications which include solution of the riddle of the double helix (for a recent review see ref. 1).

On the other hand, every attempt has been made to collect data of value to a chemist who may wish to apply molecular mechanics to specific problems. These data include tables of interaction constants (Tables 1–4) in Part A, and relatively complete groupings of calculated strain energies, in Part B, for those who may seek solutions to specific stereochemical problems (Tables 5, 7, 10, 11 and 13). Whenever data are available, we have compared observed molecular parameters (structural, thermodynamic or kinetic) with calculated parameters. Similarly, when different energy minimization calculation schemes may be compared for a given compound, these data are tabulated together.

In Part B we have attempted to offer a complete survey of molecular mechanics applications in coordination chemistry. Omissions stem from our oversight and judgement, and from cases where structural and/or molecular mechanics data are incompletely reported. All of the interaction constants, molecular dimensions and energies are reported in the traditional units of molecular mechanics: cgs, Å, and kcal mol^{-1}. These are the units of the bulk of the original reports, and also the units employed within available molecular mechanics programs, should a reader choose to perform calculations.

In Part C we briefly look ahead towards some interesting applications of molecular mechanics to problems in chemical dynamics and crystal structure analysis.

(ii) An overview of molecular mechanics calculations

The relationship between structure, reactivity and strain energy has long been recognized, but has generally been difficult to quantify. The concepts of ring strain and steric hinderance have been used to explain the course of organic [1–3] and inorganic reactions [4,5]. Ring strain and steric hinderance have often been used in a qualitative way to explain major differences in reactivity and in the distribution of reaction products. Steric arguments have been used so often that they have gained a reputation as a "catch all" term to explain differences in reactivity which cannot be explained by other differences in the reactants [6].

Early calculations

The earliest quantitative calculations of strain energy were performed by

Hill on methyl amine–methyl boron adducts [9], and by Westheimer to estimate the activation energy for the racemization of optically active biphenyls [10]. These calculations considered only the non-bonded interactions, and required only a knowledge of the van der Waals repulsion between the substituents. Both of these calculations agreed remarkably well with experimentally determined energies.

Variations of Westheimer's method were applied to various organic molecules by Allinger and others [1–3]. Work on organic systems by Allinger, Scheraga [11] and Lifson [12,13], using several calculation schemes, provided a consistent set of potential functions and interaction constants essential for the complex calculations which have been performed in recent years.

The first quantitative application of conformational analysis calculations to transition metal systems appeared in a classic paper by Corey and Bailar [14]. They employed a vector analysis method previously applied to organic systems [15] to calculate the strain energy of some simple coordination complexes with five- and six-membered rings. This technique used fixed atom positions, assumed standard bond distances and angles, calculated the non-bonded contribution and determined the most favorable conformation.

A technique applied by Gollogly and Hawkins [16] allowed atoms to move individually, sampling different energy environments, until a minimum energy was obtained. This was a significant improvement over static methods, but required a large number of iterations for even relatively simple structures, such as substituted five-membered [17] or six-membered chelate rings [18].

With the rapidly increasing availability of large computers at reasonable cost, molecular mechanics calculations have become a popular tool among organic chemists, particularly in industrial settings [7]. Inorganic chemists, however, have been somewhat slower to grasp the importance of this technique. This can be attributed, in part, to the difficulty of applying the technique to complex heteronuclear systems, which arises from the greater number of different atoms [8] for which the interactions must be modelled.

Molecular mechanics calculations provide an idealized picture of the gas phase structure of a molecule. This structure is free from lattice interactions which may affect the structure in the solid state, and solvent effects which may exist in solution. Even though solvent effects are not included in the molecular mechanics calculation, the freedom from lattice effects may allow a molecular mechanics calculation to generate a model of the solution structure superior to a structure determined by crystallography.

(iii) A description of two popular energy minimization techniques

With the increased availability of large computers at reasonable cost, extended calculations of strain energy became possible. The strain energy for

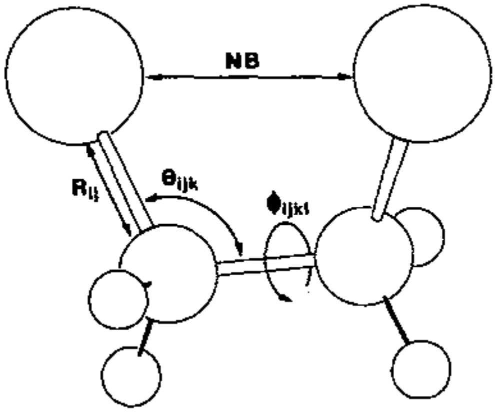

Fig. 1. Components of intramolecular strain.

a molecule is factored into the components (Fig. 1):

$$U_{\text{total}} = U_{\text{bonded}} + U_{\text{angles}} + U_{\text{torsion}} + U_{\text{non bonded}}$$

with each component described by potential functions to be described in Section A (iv).

Molecular mechanics calculations have generally employed one of two different methods for the minimization of strain energy. The first of these methods, the steepest descent method, was originally described by Wiberg [19] and applied to organic systems by Scheraga [11]. The second method is the modified Newton–Raphson method described by Boyd [20].

The steepest descent method [19] begins with the Cartesian coordinates of each atom and a set of potential functions to describe intramolecular interactions. The method requires the evaluation of a $3N$ (N is the number of atoms) dimensional vector in which each element is the partial derivative of the energy with respect to a change in one coordinate (estimated by moving the atom a small distance in one direction). The atoms are moved an amount proportional to the partial derivative, and the energy is recalculated until it no longer decreases. A new set of partial derivatives is calculated and the process continued until the minimum energy is reached.

The modified Newton–Raphson method developed by Boyd [20] uses similar internal coordinates and potential functions to describe the interactions. Boyd's technique allows all of the atoms to move in unison by applying a modified Newton–Raphson minimization scheme in which the gradient of the potential energy is expanded in a Taylor series near the equilibrium atomic positions. This procedure is only approximate, since the expansion is truncated after the second-order terms. To arrive at a minimum energy, an iterative process is used with the number of iterations depending on how accurately the initial coordinates represent the minimized geometry and how well the potential is approximated by the force field. While this technique requires a significant amount of computer time, the number of iterations is usually small. Boyd's program also has the ability to calculate thermodynamic functions and the vibrational frequencies of the minimized structure based on the final coordinates and their shifts in the final cycle of refinement.

While each of these procedures arrives at the minimum energy by an iterative procedure, Boyd's Newton–Raphson technique has been more commonly used with inorganic systems. The preference for the Newton–Raphson calculation scheme arises from the rapid convergence, especially when the trial coordinates are near the equilibrium coordinates. In contrast, given approximate atomic coordinates the steepest descent method approaches the minimum energy configuration rapidly. However, as equilibrium is approached, convergence becomes very slow. When approximate coordinates are available from known structures, the Newton–Raphson method is often found to converge more rapidly than the steepest descent method.

An initial guess for the atomic coordinates, required by either technique, can often be obtained from the crystal structure of a related compound [21]; can be estimated from an examination of molecular models [22]; or can be calculated. If the initial coordinates are far from the minimized coordinates, care must be taken to avoid local minima in the force field. The use of ORTEP [23] to produce drawings of the minimized structures is a great help in avoiding this problem.

(iv) Potential functions and the force field

The force field is a model for the potential surface on which the atoms of the molecule are located. Two different force fields are commonly used for structure calculation, the generalized valence force field (GVFF) and the Urey–Bradley force field (UBFF). For the purpose of molecular mechanics calculations, the principal difference between the two force fields is the implicit inclusion of 1–3 non-bonded interactions in the valence angle deformation force constants of the UBFF. In the GVFF, these force constants are explicitly included. A careful study by Wiberg and Boyd [24] found no major differences in the vibrational spectrum of cyclohexane calculated with a UBFF compared with the spectrum calculated with a GVFF by Wiberg and Shrake [25]. The forms of the potential functions and the interaction constants required for the model are usually available from molecular spectroscopy. The force field for a molecule is normally considered to be made up of several components (Fig. 1)

$$U_{\text{total}} = U_{\text{bonded}} + U_{\text{angles}} + U_{\text{torsion}} + U_{\text{non bonded}}$$

with each of the potential functions being described below.

Bond deformation, $U(R_{ij})$

Deformation along bonds is generally approximated by an harmonic oscillator:

$$U(R_{ij}) = 0.5k(R_{ij})(r_{ij} - r^0)^2$$

where $k(R_{ij})$ is the spectroscopic force constant for a particular bond; r_{ij} is the actual bond distance; and r^0 is the unstrained bond distance. Adequate values for $k(R_{ij})$ and r^0 can usually be obtained from vibrational spectra [26] of simple compounds and from crystal structures of related compounds, respectively. Some values for R_{ij} interaction constants are shown in Table 1. This classical potential overestimates the strain energy of bonds far from their equilibrium distance. For most structures, however, the bond distances are expected to be close to the equilibrium values.

Valence angle deformation, $U(\theta_{ijk})$

Valence angle deformations can also be described in terms of an harmonic

TABLE 1

Interaction constants for bond deformation potentials [$U(R_{ij}) = 0.5k(R_{ij})(R_{ij} - r^0)^2$]

Bond type		$k(R_{ij})$ (mdyn Å^{-1})	r^0 (A)	Ref.
I	J			
Co(III)	N	2.25	1.95	68
Co(III)	O	2.25	1.93	62
Co(III)	Cl	1.68	2.30	37
Ni(II)	N	0.68	2.10	58
Cu(II)	S	0.50	2.38	75
Cu(II)	N=	0.89	2.00	80
Cu(II)	O	0.89	2.00	75
C–	C–	4.50	1.52	68
C=	C–	4.50	1.42	20
C=	C=	7.65	1.39	20
C=	O	9.00	1.24	62
C–	H	4.55	1.09	37
N–	C–	3.89	1.47	37
N=	C=	7.65	1.35	20
N–	H	4.92	1.00	37
O	H	4.92	1.00	80
S–	C–	2.64	1.82	75

TABLE 2

Interaction constants for valence angle deformation potentials $[U(\theta_{ijk}) = 0.5k(\theta_{ijk})(\theta_{ijk} - \theta^0)^2]$

Angle type			$k(\theta_{ijk})$ (mdyn rad^{-1})	θ^0 (rad)	Ref.
I	J	K			
N	Co(III)	N	0.400	1.571	37
Cl	Co(III)	Cl	0.278	1.571	37
Cl	Co(III)	N	0.278	1.571	37
N	Ni(II)	N	0.300	1.571	58
N=	Cu(II)	N=	0.030	1.911	80
S	Cu(II)	N=	0.030	1.911	80
S	Cu(II)	S	0.030	1.911	75
Co(III)	N	C	0.278	1.911	37
Co(III)	N	H	0.278	1.911	37
Ni	N	C	0.200	1.911	58
Ni	N	H	0.100	1.911	58
Cu(II)	N=	C=	0.278	2.095	75
Cu(II)	O	H	0.278	1.911	75
Cu(II)	S	C	0.080	1.911	75
B–	C–	C–	0.800	1.937	37
C=	C=	C–	0.700	2.095	20
C=	C=	C=	1.000	2.095	20
C–	C–	H	0.605	1.911	37
C=	C=	H	0.500	2.095	20
C–	C–	N–	0.694	1.911	37
C=	C=	N=	1.000	2.095	80
C–	C–	S	0.694	1.911	75
H	C–	H	0.508	1.883	37
N–	C–	H	0.485	1.911	37
N=	C=	H	0.750	2.095	80
O	C–	H	0.378	1.911	80
S	C–	H	0.485	1.911	80
C–	N–	C–	0.694	1.911	37
C–	N–	H	0.278	1.911	37
H	N–	H	0.417	1.911	37
C–	O	C–	0.278	1.911	80
H	O	H	0.417	1.911	80
C–	S	C–	0.500	1.740	75

oscillator:

$$U(\theta_{ijk}) = 0.5k(\theta_{ijk})(\theta_{ijk} - \theta^0)^2$$

where $k(\theta_{ijk})$ is the spectroscopic angle deformation force constant and θ^0 is the unstrained angle. This function assumes that there are only small deviations (10° or less) from the unstrained angle. The force field contains one interaction for each angle in the complex.

Torsional barriers, $U(\phi_{ijkl})$ (Table 3)

The barrier to rotation about a bond can be described by a function of the

TABLE 3

Interaction constants for torsional potentials $(U(\phi_{ijkl}) = 0.5A[1 + B\cos(C\phi)])$

Atom				A (rad.)	B (rad.)	C (rad.)	Ref.
I	J	K	L				
Co(III)	N–	C–	C–	0.00151	3.000	1.047	37
Cu(II)	S	C–	C–	0.00076	3.000	1.047	75
Cu(II)	S	C–	H	0.00151	3.000	1.047	75
Cu(II)	O	C	C	0.00076	3.000	1.047	80
Cu(II)	O	C	H	0.00076	3.000	1.047	80
H	C	C	H	0.00151	3.000	1.047	37
C	C	C	H	0.00227	3.000	1.047	37
C	C	C	N	0.00114	3.000	1.047	37
C=	C	C	H	0.00227	3.000	1.047	20
C=	C	C	O	0.00151	3.000	1.047	20
N	C	C	H	0.00227	3.000	1.047	37
N	C	C	N	0.00114	3.000	1.047	37
S	C	C	H	0.00227	3.000	1.047	75
S	C	C	C=	0.00114	3.000	1.047	80
S	C	C	O	0.00151	3.000	1.047	80
S	C	C	S	0.00076	3.000	1.047	75
C=	C=	C=	C=	0.08000	2.000	0.000	20
C=	C=	C=	N=	0.08000	2.000	0.000	22
H	C=	C=	H	0.08000	2.000	0.000	20
H	C	N	C	0.00151	3.000	1.047	37
H	C	N	H	0.00100	3.000	1.047	37
C	C	N	H	0.00151	3.000	1.047	37
C	C	N	C	0.00076	3.000	1.047	37
C	C	O	H	0.00151	3.000	1.047	75
H	C	O	H	0.00151	3.000	1.047	65
C	C	S	C	0.00076	3.000	1.047	75
H	C	S	C	0.00151	3.000	1.047	75

$U(\delta_{ijkl}) = k(\delta_{ijkl})*\delta$

I	J	K	L	$k(d_{ijkl})$	Ref.
C=	N=	C=	Cu(II)	0.70000	75
Cu(II)	N=	C=	C	0.29000	75
C=	C=	C=	H	0.29000	20
C=	C=	C=	C–	0.70000	20
N=	C=	C=	H	0.29000	22
C–	C=	C=	H	0.29000	20

type:

$$U(\phi_{ijkl}) = 0.5k(\phi_{ijkl})[1 + \cos(n\phi)]$$

where $k(\phi_{ijkl})$ is the energy barrier to rotation around the bond; ϕ is the displacement of the dihedral angle from an "ideal" value (60° or 1.047 rad. for bonds between tetrahedral atoms, etc.); and n is the periodicity (3-fold for bonds between tetrahedral atoms). $k(\phi_{ijkl})$ is estimated from rotation barriers determined spectroscopically for small molecules such as ethane and methylamine, and 1,4 non-bonded components are omitted. The torsional interactions around the metal ion are generally not included in the force field because of their higher periodicity and the presumed small amplitude of the interaction.

A second potential function related to $U(\phi_{ijkl})$ is the function $U(\delta_{ijkl})$ which takes the form

$$U(\delta_{ijkl}) = k(\delta_{ijkl})\,\delta$$

where $k(\delta_{ijkl})$ is the force constant and δ is the distance of atom L from the plane defined by atoms I, J and K. This potential is used to describe the deviations of substituents on an aromatic ring from the plane of the aromatic ring.

Non-bonded interactions, $U(\mathrm{NB})$

Non-bonded interactions are usually described by one of the two potential functions,

$$U(\mathrm{NB}) = -C/r^6 + A/r^{12} \text{ Lennard–Jones Potential [27]}$$

or

$$U(\mathrm{NB}) = -C/r^6 + A\exp(-Br) \text{ Buckingham Potential [28]}$$

where A, B, C and D are estimated from virial coefficients and van der Waals radii for simple gases, and r is the distance between the atoms. Both of these potential functions show a small attractive component at large distances and a large repulsive term at shorter distances. In practice, non-bonded interactions (in units appropriate to erg molecule^{-1}) have been calculated from Hill's equations [29]:

$$A = 8.28 \times 10^5\epsilon^{12}/144$$

$$B = 1/\left[(r^*_i + r^*_j) \times 0.0736\right]$$

$$C = -2.25 \times (r^*_i + r^*_j)^6 \times \epsilon_{12}/144$$

TABLE 4

Interaction constants for non-bonded potentials $[U(\mathrm{NB}) = A \exp(-Br_{ij}) + Cr_{ij}^{-6}]$

Atom		10^{11}A, erg molecule	B, Å	10^{11}C, ergÅ^{-6} molecule
I	J			
H	H	375.0	4.685	0.604
H	B	398.4	4.614	0.706
H	C	363.7	4.383	0.877
H	C=	363.7	4.484	9.765
H	N	481.1	4.544	0.934
H	N=	481.1	4.653	0.810
H	O	498.0	4.572	0.932
H	F	514.3	4.558	0.981
H	S	909.2	4.117	3.191
H	Cl	883.3	4.044	3.454
H	Co(III)	995.9	3.973	4.330
H	Cu(II)	1036.6	3.950	4.668
B	B	276.0	4.544	0.536
B	C	252.0	4.320	0.663
B	C=	252.0	4.419	0.579
B	N	333.3	4.477	0.708
B	N=	333.3	4.582	0.615
B	O	345.0	4.503	0.707
B	F	356.3	4.490	0.743
B	S	629.9	4.062	2.398
B	Cl	612.0	3.990	2.592
B	Co(III)	690.0	3.921	3.245
B	Cu(II)	718.2	3.899	3.496
C	C	230.0	4.117	0.807
C	C=	230.0	4.206	0.710
C	N	304.3	4.259	0.871
C	N=	304.3	4.355	0.763
C	O	314.9	4.283	0.872
C	F	325.3	4.271	0.916
C	S	575.0	3.882	2.872
C	Cl	558.7	3.817	3.090
C	Co(III)	629.9	3.753	3.852
C	Cu(II)	655.6	3.733	4.144
C=	C=	230.0	4.300	0.622
C=	N	304.3	4.355	0.763
C=	N=	304.3	4.455	0.666
C=	O	314.9	4.380	0.762
C=	F	325.3	4.367	0.801
C=	S	575.0	3.961	2.544
C=	Cl	558.7	3.893	2.743
C=	Co(III)	629.9	3.827	3.426
C=	Cu(II)	655.6	3.806	3.688
N	N	402.5	4.411	0.934

TABLE 4 (continued)

Atom		10^{11}A, erg molecule	B,Å	10^{11}C, ergÅ^{-6} molecule
I	J			
N	N=	402.5	4.514	0.813
N	O	416.6	4.437	0.933
N	F	430.3	4.424	0.981
N	S	760.7	4.008	3.137
N	Cl	739.0	3.938	3.386
N	Co(III)	833.3	3.871	4.234
N	Cu(II)	867.3	3.849	4.560
N=	N=	402.5	4.621	0.706
N=	O	416.6	4.541	0.812
N=	F	430.3	4.527	0.854
N=	S	760.7	4.092	2.768
N=	Cl	739.0	4.020	2.995
N=	Co(III)	833.3	3.950	3.752
N=	Cu(II)	867.3	3.927	4.044
O	O	431.3	4.464	0.932
O	F	445.4	4.450	0.980
O	S	787.4	4.029	3.145
O	Cl	765.0	3.959	3.397
O	Co(III)	862.5	3.891	4.250
O	Cu(II)	897.7	3.869	4.577
F	F	460.0	4.437	1.030
F	S	813.2	4.019	3.301
F	Cl	790.1	3.949	3.564
F	Co(III)	890.8	3.881	4.457
F	Cu(II)	927.2	3.859	4.801
S	S	1437.5	3.672	10.022
S	Cl	1396.7	3.614	10.724
S	Co(III)	1574.7	3.557	13.296
S	Cu(II)	1639.0	3.538	14.280
Cl	Cl	1357.0	3.557	11.458
Cl	Co(III)	1530.0	3.502	14.185
Cl	Cu(II)	1592.4	3.484	15.227

where

$$\epsilon_{12} = (\epsilon_1\epsilon_2)^{1/2}$$

Some non-bonded interaction constants applicable to the study of transition metal complexes are given in Table 4.

(v) Other considerations

In inorganic chemistry, molecular mechanics calculations have been applied primarily to stereochemical problems in the chemistry of cobalt(III) amine complexes. The problems addressed using this technique have usually been those of structure and its relationship to isomer distributions and thermodynamic or kinetic stability.

Molecular mechanics calculations do not serve as a replacement for experimental methods for structure determination, but as a complementary technique. For example, X-ray crystallography is often taken as the ultimate method for determining the structure of coordination compounds. Hydrogen atom positions are, however, often calculated and generally not refined. Yet non-bonded interactions involving hydrogen atoms have been found to be a large, often primary, contributor to the total strain energy of a molecule. In addition, crystallographically determined structures of different crystals of the same cationic complex ($[Co(en)_3]^{3+}$, Table 6) often differ significantly in detail, suggesting that lattice effects are important in many, if not all, cases. Indeed, the magnitude of lattice effects may be estimated from the energy differences between the observed conformer and other likely (and often lower energy) conformers. In many cases, these energy differences are small (< 3 kcal mol^{-1}).

Nuclear magnetic resonance has also been extensively used to study structures of inorganic compounds; interpretation of NMR spectra can be

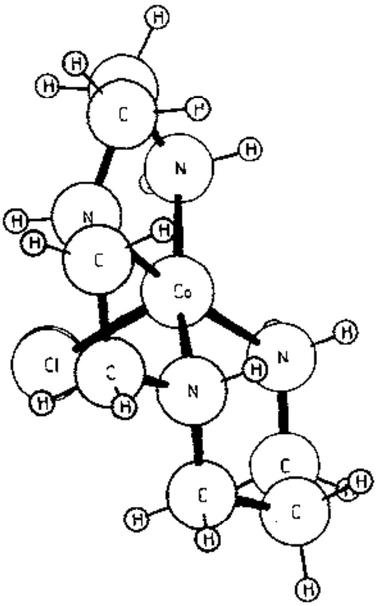

Fig. 2. super *cis* $[Co(2,2,3\text{-tet})Cl_2]^+$. Note two chloride ions on one side of the Co–N_4 plane. In the UBFF model, 1–3 non-bonded interactions are implicit in the angle deformation parameters. In this calculation, nominal 180° angles are deleted to prevent accidental cos(180) calculation overflow. Together, the result was this improbable structure.

greatly simplified if the details of the structure are known. Strain energy minimization calculations have been shown to play an important role in the interpretation of NMR spectra [30–35].

In a recent series of papers, Hambley and co-workers [33–35] have taken crystal coordinates as the starting point for energy minimization calculations of ligand conformers, and used these results to assist in the interpretation of ^{1}H-NMR spectra. They have shown that the population of conformers separated by small energy differences may be estimated from Karplus relationships. Hawkins [30] has recently reviewed applications of NMR spectroscopy to the conformational analysis of transition metal complexes.

Caution should be exercised in the comparison of energies for various minimized structures. Different assumptions, particularly in the force field and in convergence criteria, make significant differences in the calculated strain energies. Care must also be exercised in order to avoid false minima on the potential surface. One example of a false minimum is shown in Fig. 2. The complex *trans* $[Co(2,2,3\text{-tet})Cl_2]^+$ easily minimized to this structure due to an error in the coordinates which was not corrected in the UBFF. In many cases, false minima can be detected by examining the ORTEP drawing of the calculated structure.

B. A SURVEY OF MOLECULAR MECHANICS CALCULATIONS IN COORDINATION CHEMISTRY

In inorganic chemistry, molecular mechanics calculations have been most often applied to stereochemical problems in the chemistry of cobalt(III) amine complexes. The problems addressed are typically those of structure and its relationship to isomer distributions and thermodynamic or kinetic stability.

(i) Complexes with bidentate ligands

(a) Five-membered chelate rings

The initial studies of five-membered chelate rings by Corey and Bailar [14] indicated a preference for the puckered arrangement over planar or envelope conformations. The puckering angle determined in this study was 48.8°, resulting in a N–M–N bond angle of 85.8°. Calculations by Gollogly and Hawkins [17] produced similar conformational energies, but indicated a range of solutions for small variations in the metal–donor distances and angles, consistent with the range found experimentally [36].

Cobalt(III) complexes of the form $[Co(en)Cl_4]^-$ have been studied by DeHayes and Busch [37] using the method of Boyd [20]. The chief sources of strain within the ethylenediamine ring of $[Co(en)Cl_4]^-$ were found to be small deviations in the carbon and nitrogen bond angles from the tetrahedral bond angle of 109.5°, and in the torsion angles around the C–N bonds. Another significant source of strain, not apparent from the totals (strain energies for diamine complexes are shown in Table 5), are the non-bonded repulsions between axial methylene and equatorial amine protons, and those between equatorial methylene and axial amine protons. While the majority of the non-bonded interactions are small attractive forces, these repulsive interactions represent about 0.36 kcal mol^{-1} each. The significance of non-bonded interactions involving amine protons is dramatically illustrated by a comparison of the strain energies of amine complexes with thiol and thiaether analogues.

Replacement of one of the C–H protons with a methyl group, studied first by Gollogly and Hawkins [16] and later by DeHayes and Busch [37], demonstrates the energy difference between axial and equatorial substitution on a five-membered chelate ring. Equatorial substitution serves to decrease the total strain energy, primarily due to an overall decrease in non-bonded interactions. Axial substitution, however, increases the strain energy due to a flattening of the chelate ring and an increase in the non-bonded interactions around the methyl group. Multiple substitution at the carbon atoms produces effects which are roughly additive.

Methyl substitution at the amine nitrogen is shown to increase the strain energy by 1–1.2 kcal mol^{-1}, depending on the orientation of the methyl group. This increase is due primarily to increases in Co–N and N–C bond distances and to increased non-bonded interactions between the methyl groups and the chlorine atoms of $[Co(am)Cl_4]^-$. Hambley et al. [33] have reported a detailed crystallographic, NMR and molecular mechanics study of N- and C-substituted diamine chelate rings in complexes of Co(III) and Pt(II). Among the unique aspects of this study are the use of a modification of Boyd's algorithm in which 1–3 non-bonded interactions at the metal ion are subsitituted for metal valence angle deformations, and the inclusion of a square planar Pt(II) center. The former modification, together with a general adjustment of valence angle force constants, provides for some asymmetry in these potentials, and also allows some freedom in dealing with force constants which are often ambiguously assigned.

Calculation of the strain energy at a square planar center, using only 1–3 non-bonded interactions to model valence angle deformations at the metal, results in a tetrahedral bias in the calculated coordination environment. This was offset by including "phantom" hydrogen atoms along the tetragonal axis to simulate the axial electron density in a planar d^8 complex.

In this calculation, the complex $[Pt(3,3\text{-}(CH_3)_2\text{-}1,2\text{-butanediamine})(2,2\text{-dipyridine})]^{2+}$ was modelled without using the "delta", or aromatic out-of-plane deformation potential (vide supra). The ethylenic force constants within the

TABLE 5

Calculated intramolecular strain energies for some diamine complexes with five-membered chelate rings

Complex [a]	R_{ij}	θ_{ijk}	ϕ_{ijkl}	NB	Total	Ref.
$[Co(en)Cl_4]^-$	0.25	1.25	0.60	−1.51	0.58	37
$[Co(pn)Cl_4]^-$(eq)	0.29	1.34	0.58	−2.59	−0.38	37
$[Co(pn)Cl_4]^-$(ax)	0.41	1.95	1.30	−1.85	1.81	37
$[Co(bn)Cl_4]^-$(eq,eq rac)	0.37	1.66	0.76	−3.53	−0.75	37
$[Co(bn)Cl_4]^-$(eq,ax meso)	0.53	2.54	1.31	−2.77	1.68	37
$[Co(bn)Cl_4]^-$(ax,ax rac)	0.63	3.20	2.11	−2.11	3.77	37
$[Co(N{-}CH_3{-}en)Cl_4]^-$(eq)	0.56	2.50	0.50	−1.08	2.49	37
$[Co(N{-}CH_3{-}en)Cl_4]^-$(ax)	0.55	2.22	0.93	−1.06	2.63	37
trans-N(*S*),C(*R*) $[Co(en)_2(N{-}CH_3{-}Ala)]^{2+}$	0.93	3.13	4.09	−2.86	5.3	43
trans-N(*R*),C(*S*) $[Co(en)_2(N{-}CH_3{-}Ala)]^{2+}$	0.94	3.63	4.47	−2.71	6.3	43
cis-N(*S*)-C(*S*) $[Co(en)_2(N{-}CH_3{-}Ala)]^{2+}$	1.11	4.17	3.12	−1.78	6.6	43
cis-N(*R*),C(*R*) $[Co(en)_2(N{-}CH_3{-}Ala)]^{2+}$	1.15	5.15	4.60	−1.81	9.1	43
$[Co(en)_3]^{3+}$	1.33	3.47	2.78	6.53	14.09	79

[a] Abbreviations: ethylenediamine = en; 1,2-diaminopropane = pn; 2,3-diaminobutane = bn; and 1-amino-3-azabutane = *N*-methylethylenediamine=*N*-CH_3-en.

bipyridine ligand were increased sufficiently to reproduce observed structural features.

In this study, crystallographic coordinates were used to initialize the strain energy calculation, which was used to estimate the energies and N–C–C–N torsion angles for axial and equatorial substituents. The observed $^3J_{H-H}$ coupling constants were interpreted to yield the mole fractions of axial- and equatorial-substituted chelate rings for various combinations of substituents.

The effect of multiple substitution in other complexes is summarized in Table 5.

Early calculations of the conformation of bis(ethylenediamine) complexes by Corey and Bailar [14] showed the importance of inter-ring interactions on the conformation of *trans* bis(ethylenediamine) complexes (Fig. 3). The energy difference between the meso and racemic *trans* complexes was estimated at 1 kcal mol^{-1} with the racemate at lower energy. These calculations were based on fixed-ring systems (vide supra) which did not allow the non-bonded interactions to be distributed throughout the chelate ring system.

Subsequent calculations by Gollogly and Hawkins [16] distributed the

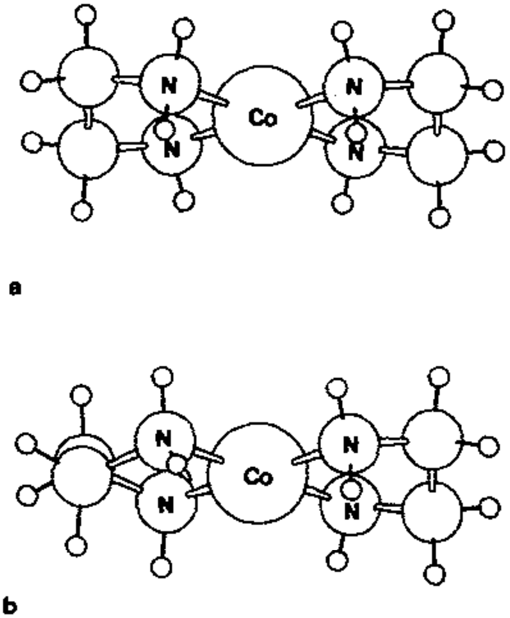

Fig. 3. Relative conformations of *trans* bis(ethylenediamine) chelate rings. (a) (C_{2h}); (b) (C_2).

strain energy in the chelate rings. In this case the strain energies of the meso and racemic *trans* isomers were identical, consistent with the crystallographic determination of the meso complex [38]. The calculated strain energies of the two *cis* conformers were also nearly equal, consistent with the variety of isomers observed in the solid state [39,40].

Strain energy minimization studies of the isomers of Δ[Co(enλ)(enδ)-(N–CH$_3$–Ala)]$^{2+}$ by Buckingham et al. [43], also using Boyd's method, successfully reproduced the crystallographic structure, predicted the correct energy ordering of the isomers, and accounted for the observed isomer ratios. Moreover, some of the more subtle features of the X-ray structure were also contained in the calculated structure. For example, the lengthening of the bond between cobalt and the alanine nitrogen (barely significant crystallographically) was accurately reproduced in the calculated structure; flattening of the ethylenediamine chelate ring was also reproduced in the calculated structure. A detailed comparison of observed and calculated bond angles and distances is given in Table 6.

Conformational analysis of [Co(en)$_2$(N–CH$_3$–Ala)]$^{2+}$ also illustrates the importance of inter-ring interactions in determining the final structure. In addition to the interactions described in the single-ring model, there are several important interactions between the chelate rings of this complex. These inter-ring interactions are expected to result in distortion of the

TABLE 6

Comparison of selected observed and calçulated bond distances and angles for some diamine cobalt(III) complexes

Distance or angle	$[Co(en)_2(N–CH_3–(S)–Ala)]^{2+}$		$[Co(en)_3]^{3+}$		
	X-ray [a]	Calc.	X-ray [b]	X-ray [c]	Calc. [d]
Co–N	1.969	1.98	1.947	1.960	1.98
Co–N	1.940	1.98	1.956	1.970	1.98
Co–N	1.954	1.97	1.964	1.955	1.98
Co–N	1.955	1.97	1.967	1.959	1.98
Co–N			1.967	1.967	1.98
Co–N			1.981	1.965	1.98
N–C	1.46	1.49	1.480	1.488	1.48
C–C	1.53	1.50	1.526	1.498	1.52
C–N	1.49	1.49	1.468	1.488	1.48
N–C	1.50	1.50	1.466	1.488	1.48
C–C	1.53	1.50	1.494	1.503	1.52
C–N	1.46	1.50	1.464	1.499	1.48
N–C			1.459	1.491	1.48
C–C			1.457	1.493	1.52
C–N			1.489	1.494	1.48
N–Co–N	84.6	86.7	85.9	85.6	86.5
N–Co–N	85.0	87.8	85.2	85.6	86.5
N–Co–N			85.2	85.6	86.5
Co–N–C	110.5	108.6	110.1	109.5	108.1
N–C–C	107.4	107.9	106.9	107.4	107.4
C–C–N	104.0	107.7	109.5	107.4	107.5
C–N–Co	109.9	106.6	107.0	109.5	108.1
Co–N–C	111.4	108.9	107.7	109.5	108.1
N–C–C	108.3	109.3	106.7	107.4	107.5
C–C–N	106.9	109.4	106.6	107.4	107.5
C–N–Co	110.6	107.3	111.3	109.5	108.1
Co–N–C			110.1	109.5	108.0
N–C–C			108.7	107.4	107.4
C–C–N			108.0	107.4	107.5
N–C–Co			108.5	109.5	108.1

[a] Ref. 41. [b] ref. 42. [c] ref. 43. [d] ref. 79.

structure, especially when multiple substituents are present.

Molecular mechanics calculations on tris(diamine)cobalt(III) complexes have yielded structures similar to those calculated for simpler systems. Crystallographic studies of tris(ethylenediamine) complexes of Co(III), Ni(II), Ru(II) and Ru(III) [44] have shown that the occurrence of the (δ, δ, λ) and (δ, δ, δ) conformations depends on details of hydrogen bonding in a particular crystal. For metal–donor distances of about 2 Å, the energy difference between these conformers favors the (δ, δ, λ) conformation by about 0.15 kcal mol^{-1}. In Table 6, observed bond angles and distances for $[Co(en)_3]^{3+}$ [42,43], are compared with angles and distances calculated using Boyd's method. Niketic et al. [45,46] calculated the conformational energies of $[Co(bn)_3]^{3+}$ using the steepest descent method. Similar calculations were performed by Tapscott et al. [47], using Boyd's algorithm. While the structural parameters found in the latter work were consistent with previous work [48], the isomer distribution did not agree well with experiment. The poor agreement between experiment and calculations was ascribed to environmental effects, such as solvent interactions and non-equilibrium conditions.

(b) Six-membered chelate rings

The pioneering studies of Corey and Bailar [14] indicated an energetic preference for the chair chelate ring conformation over either the boat or skew-boat conformations. More elaborate calculations by Gollogly and Hawkins, using a unique computational method (vide supra), and by Niketic and Woldbye [49] using the steepest descent method, suggest a significant flattening of the chair to alleviate some of the strain.

DeHayes and Busch [37] studied a series of cobalt complexes with six-membered chelate rings. They considered each of the basic ring conformations, chair, skew-boat (twist) and boat. The boat conformation was found to be much higher in energy, consistent with previous work on cyclohexane [50]. The chair and skew-boat conformations were found to be significantly different from the ethylenediamine system [37], with longer Co–N bond lengths, and angles in the aliphatic ring greater than the "ideal" tetrahedral bond angle of 109.5°. Even the N–Co–N bond angle was greater than the expected 90°.

The chair and skew-boat conformations were found to have similar contributions from bond deformation, valence angle deformation and from non-bonded repulsion. The skew-boat conformer had, however, 1.6 kcal mol^{-1} of additional torsional strain energy, resulting principally from flattening of the chelate ring. Thus, in the chair form the torsion angles are very near the expected 60° while in the twist conformer the average torsional angle is 38°. Strain energy minimization calculations on the 1,3-diaminobutane chelate ring showed that methyl substitution on the carbon, in an equatorial orientation, causes very little change in a chelate ring conformation. An axial methyl group, however, causes many of the same changes observed in the five-membered chelate ring. It was noted that an increase in energy of 2.6 kcal mol^{-1} accompanies the change from an equatorial to an axial methyl group (Table 7). The effect of an axial methyl group is reflected in a flattening of the chelate ring to alleviate some non-bonded interactions between the methyl group and the axial protons and chlorides of

TABLE 7

Calculated intramolecular strain energies for some diamine complexes with six-membered chelate rings

Complex [a]	R_{ij}	θ_{ijk}	ϕ_{ijkl}	NB	Total	Ref.
$[Co(tn)Cl_4]^-(\gamma)$	0.54	3.07	0.14	−0.21	3.55	37
$[Co(tn)Cl_4]^-(\delta)$	0.41	2.90	1.70	−0.28	4.73	37
$[Co(1,3\text{-}bn)Cl_4]^-(\gamma,eq)$	0.62	3.17	0.15	−1.14	2.80	37
$[Co(1,3\text{-}bn)Cl_4]^-(\gamma,ax)$	0.81	5.08	1.28	−0.14	7.03	37
$[Co(1,3\text{-}bn)Cl_4]^-(\delta,eq)$	0.61	2.89	1.70	−1.43	3.77	37
$[Co(1,3\text{-}bn)Cl_4]^-(\delta,ax)$	0.82	5.50	2.65	−0.30	8.67	37
$[Co(N\text{-}CH_3\text{-}tn)Cl_4]^-(\gamma,eq)$	0.96	4.62	0.17	0.16	5.90	37
$[Co(N\text{-}CH_3\text{-}tn)Cl_4]^-(\gamma,ax)$	0.97	4.88	0.27	0.26	6.39	37
$[Co(N\text{-}CH_3\text{-}tn)Cl_4]^-(\delta,eq)$	1.04	4.14	1.76	0.32	7.26	37
$[Co(N\text{-}CH_3\text{-}tn)Cl_4]^-(\delta,ax)$	0.65	4.73	1.67	0.05	7.09	37
$[Co(2,4\text{-}ptn)(NH_3)_4]^{3+}$(chair)	3.04	3.61	0.45	8.16	15.26	35
$[Co(2,4\text{-}ptn)(NH_3)_4]^{3+}$(skew-boat)	2.81	1.62	1.72	7.14	13.29	35
cis$[Co(tn)_2CO_3]^+$(AB)	1.98	4.36	0.51	7.12	13.97	52
cis$[Co(tn)_2CO_3]^+$(AA)	2.28	6.43	0.72	7.32	16.74	52
cis$[Co(tn)_2CO_3]^+$(BB)	1.87	2.63	0.35	7.09	11.95	52
$[Co(tn)_3]^{3+}(chair)_3$	4.25	10.88	2.09	11.77	28.98	52
	2.57	8.89	1.07	2.75	15.15	49
	3.86	11.71	2.07	8.62	26.27	this work
$(lel)_3$	3.30	5.02	6.02	13.87	28.21	52
	1.11	3.68	7.36	1.34	13.49	49
$(ob)_3$	5.10	6.90	5.99	16.04	34.04	52
	2.55	4.19	7.72	3.71	18.19	49
$[Co(2,4\text{-}ptn)_3]^{3+}(lel)_3$	2.06	3.51	7.70	−0.38	12.63	49
$(ob)_3$	4.78	2.21	8.04	4.40	19.44	49

[a] Abbreviations: tn = 1,3-diaminopropane; 1,3-bn = 1,3-diaminobutane; N-CH_3-tn = N-methyl-1,3-diaminopropane; and 2,4-ptn = 2,4-diaminopentane.

$[Co(1,3\text{-}bn)Cl_4]^-$. Hambley et al. [35] recently reported a crystal structure determination, strain energy minimization and ^1H-NMR study of $[Co(R,R\text{-}ptn)(NH_3)_4]^{3+}$ which compared the λ skew-boat and chair conformations; an energy difference of 1.97 kcal mol^{-1} was found.

Methyl substitution on nitrogen produces a difference of 0.62 kcal mol^{-1} between the equatorial and axial orientations, consistent with some earlier experimental work on platinum complexes [51].

Complexes with two six-membered chelate rings in the *trans* configuration, studied by Gollogly and Hawkins [18], only exhibited small differences in the calculated energies of the two chair isomers (Fig. 4). The isomer with two chelate rings on the opposite side of the plane containing the donor atoms [(a) of C_{2h} symmetry] was found to be more stable by 0.5 kcal mol^{-1}

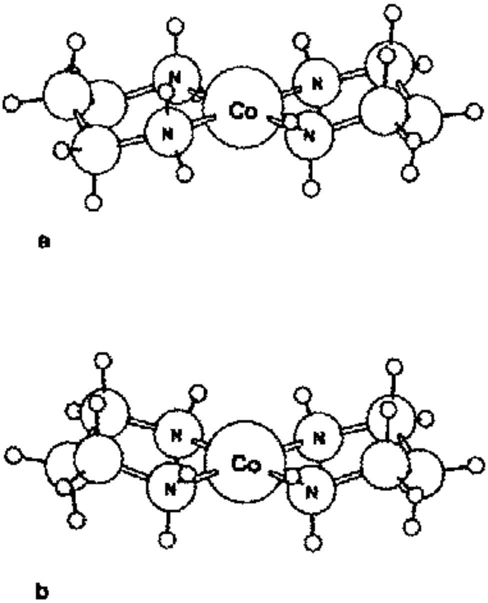

Fig. 4. Relative conformations of *trans* bis(trimethylenediamine) chelate rings. (a) C_{2h}; (b) C_{2v}.

than isomer (b) of C_{2v} symmetry, due to smaller non-bonded repulsions between the amine protons.

Complexes with two *cis* six-membered chelate rings have been studied by Geue and Snow [52] using Boyd's technique together with crystallographic methods. The crystal structure of *cis*-$[Co(tn)_2CO_3]^+$ is consistent with the lowest energy calculated structure (Table 8). The crystal structure of *cis*-$[Co(tn)_2CO_3]^+$ and the energy minimization calculations agree, even though the isomer found in the crystal study is not the lowest energy isomer. The isomer found does not have two-fold symmetry; one ring is flattened much more than the other. This conformation is intermediate in stability between the two symmetric structures, indicating the importance of crystal packing forces in molecular conformations. This study also showed the importance of inter-ring interactions in determining the overall conformation of the molecule [53].

Another study of *cis*-bis(1,3-diaminopropane)cobalt(III) complexes by Dwyer et al. [54] suggests that the symmetry of a molecule can be used to reduce the computer memory and time requirements for a molecular mechanics calculation. This study, using an adaptation of Boyd's program, showed no significant differences between the unconstrained and symmetry-constrained calculations, yet a significantly smaller core was required for the latter. This simplification has not been used often, owing to the rapidly decreasing cost of computer time and the low symmetry of many stereochemically interesting complexes.

TABLE 8

Comparison of selected observed and calculated bond distances and angles for some diamine cobalt(III) complexes with six-membered chelate rings

Distance or angle	$[Co(tn)_2CO_3]^+$		$[Co(tn)_3]^{3+}$			$[Co(ptn)_3]^{3+}$	
	X-ray [a]	Calc.	X-ray [b]	Calc. [c]	Calc. [d]	X-ray [e]	Calc. [c]
Co–N	1.97	nr [f]	1.969	2.06	1.99	1.986	2.04
Co–N	1.97	nr	1.979	2.05	2.00	1.981	2.04
Co–N	1.95	nr	1.966	2.06	1.99	1.989	2.04
Co–N	1.94	nr	1.999	2.05	2.00	1.986	2.04
Co–N			1.976	2.06	1.99	1.981	2.04
Co–N			1.984	2.05	2.00	1.989	2.04
N–C	1.53	nr	1.484	1.48	1.49	1.490	1.48
C–C	1.51	nr	1.505	1.54	1.53	1.521	1.55
C–C	1.47	nr	1.408	1.54	1.53	1.533	1.55
C–N	1.44	nr	1.471	1.48	1.49	1.484	1.48
N–C	1.49	nr	1.498	1.48	1.49	1.493	1.48
C–C	1.51	nr	1.505	1.54	1.53	1.551	1.55
C–C	1.47	nr	1.487	1.54	1.53	1.515	1.55
C–N	1.49	nr	1.488	1.48	1.49	1.490	1.48
N–C			1.477	1.48	1.49	1.484	1.48
C–C			1.507	1.54	1.53	1.521	1.55
C–C			1.492	1.54	1.53	1.533	1.55
C–N			1.485	1.48	1.49	1.493	1.48
N–Co–N	91.9	91.8	89.3	89.4	92.9	89.1	89.1
N–Co–N	89.7	88.1	89.9	89.4	92.9	88.9	89.1
N–Co–N			92.0	89.4	92.9	89.0	89.1
Co–N–C	121.2	120.2	122.0	120.3	121.4	118.0	113.5
N–C–C	107.6	111.9	110.6	112.0	111.3	112.3	111.5
C–C–C	113.8	111.2	118.8	110.5	110.2	117.5	113.4
C–C–N	112.5	111.6	118.7	111.1	113.0	112.0	111.5
C–N–Co	120.2	117.8	123.2	120.1	124.4	118.9	113.4
Co–N–C	117.5	113.9	121.1	120.3	121.4	117.2	113.5
N–C–C	110.3	111.5	111.8	112.0	111.3	111.6	111.5
C–C–C	112.7	112.3	114.1	110.5	111.2	116.9	113.4
C–C–N	111.9	111.8	113.2	111.1	112.4	112.3	111.5
C–N–Co	115.8	112.2	122.0	120.1	124.5	118.9	113.4
Co–N–C			122.6	120.3	121.4	118.0	113.5
N–C–C			112.2	112.0	111.3	112.3	111.5
C–C–C			113.0	110.5	112.2	117.5	113.4
C–C–N			111.8	111.1	112.4	111.6	111.5
N–C–Co			122.3	120.1	124.4	117.2	113.5

[a] Ref. 52. [b] Ref. 55. [c] Ref. 51. [d] This work. [e] Ref. 57. [f] Not reported.

Studies of tris(1,3-diaminopropane)cobalt(III) complexes by Gollogly and Hawkins [18] suggested that the tris chair should be the most stable conformation, in agreement with the known structure of the cobalt(III) complex [55], but in disagreement with a previous study by Woldbye [56] which suggested a preference for the tris skew-boat arrangement. Niketic and Woldbye [49], using the steepest descent method, Geue and Snow [52] and the present authors, using Boyd's method, have calculated the energies for the different possible conformers, noting that the stable conformation was dependent on the chosen force field model. Observed [55] and calculated [49] bond angles and distances for $[Co(tn)_3]^{3+}$ are compared in Table 8.

Calculations of the strain energy of tris-[(R,R)-2,4-diaminopentane]-cobalt(III) complexes by Niketic and Woldbye [45] suggested a preference for the tris skew-boat conformation which allowed the two methyl groups of each chelate ring to be in equatorial positions. The energies of the other conformations were found to increase with the number of axial methyl groups because of increased inter-ring interactions. The crystal structure of (−)-tris-(R,R-2,4-diaminopentane)cobalt(III) chloride [59] also shows the chelate rings in a skew-boat conformation with all methyl groups equatorially oriented. Observed [57] and calculated [45] bond angles and distances for this complex are compared in Table 8.

An interesting application of molecular mechanics calculations is in the prediction of the thermodynamic stability of metal complexes [58]. In the

TABLE 9

Strain energies and heats of formation for some Ni(II) complexes with polyamines

Complex [a]	Strain energy [b]	ΔStrain energy	ΔH [c]	ΔΔH
$[Ni(en)(H_2O)_4]^{2+}$	1.14		−9.0	
$[Ni(tn)(H_2O)_4]^{2+}$	3.044	1.53	−7.8	1.2
$[Ni(en)_2(H_2O)_2]^{2+}$	3.35		−18.3	
$[Ni(tn)_2(H_2O)_2]^{2+}$	7.16	3.07	−15.0	3.3
$[Ni(en)_3]^{2+}$	4.57		−28.0	
$[Ni(tn)_3]^{2+}$	13.12	7.44	−21.3	6.7
$[Ni(dien)(H_2O)_3]^{2+}$	6.08		−11.9	
$[Ni(dptn)(H_2O)_3]^{2+}$	8.28	1.46	−10.6	1.3
$[Ni(dien)_2]^{2+}$	11.87		−25.3	
$[Ni(dptn)_2]^{2+}$	21.32	7.97	−17.6	7.7

[a] For the polyamines shown, the first member of the series has all five-membered chelate rings and the second has all six-membered chelate rings. Abbreviations: en = ethylenediamine; tn = 1,3-diaminopropane; dien = 1,5-diamino-3-azapentane; and dptn = 1,7-diamino-4-azaheptane. [b] From Ref. 59. [c] From R.M. Smith and A.E. Martell. Critical Stability Constants, Vol. 2, Plenum Press, New York, 1975.

case of cobalt(III), reliable thermodynamic data are often not available due to the kinetic inertness of the complexes. Nickel complexes with five- and six-membered chelate rings show differences in the enthalpy of formation which are very similar in magnitude to the differences in strain energy. In these complexes, increased strain energy arises primarily from increased bond lengths, bond angles and non-bonded interactions. Thermodynamic enthalpies of formation, after correction for different numbers of methylene groups, differ by less than 10% from the differences in strain energy for a variety of diamine and polyamine nickel(II) complexes [59] (Table 9).

(ii) Complexes with terdentate ligands

(a) Diethylenetriamine

The only triamine complexes have been studied are the cobalt(III) complexes of diethylenetriamine. A preliminary study [60] places the energy of the *trans*, s-*cis* and uns-*cis* stereoisomers at 17.6, 17.2 and 17.2 kcal mol^{-1}, respectively. A second study applied the technique of symmetry-constrained refinement [54], arriving at the same structure as the symmetry-independent calculation of the structure [52].

(iii) Complexes with tetradentate ligands

(a) Triethylenetetraamine

Molecular mechanics calculations have been carried out on the *trans* isomers of $[Co(trien)(NH_3)_2]^{3+}$ [61] (Fig. 5). Both the racemic and *meso* isomers are high in strain energy, consistent with the experimental observation that *trans* isomers are minor products. Though the energy difference of 0.83 kcal mol^{-1} is small, it is sufficient to account for the experimental observation of both isomers.

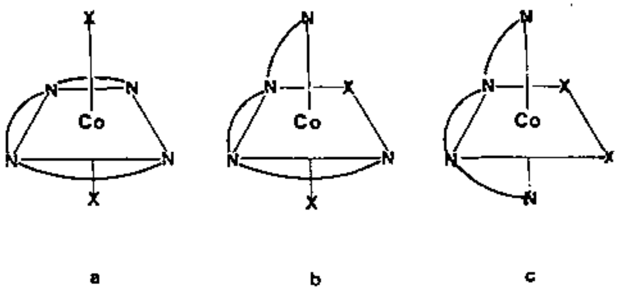

Fig. 5. Geometrical isomers of complexes with flexible tetradentate ligands. (a) *trans*; (b) uns-*cis*; (c) s-*cis*.

TABLE 10

Calculated strain energies (kcal mol^{-1}) for some cobalt(III) tetraamine complexes

Complex [a]	$U(\mathrm{R}_{ij})$	$U(\theta_{ijk})$	$U(\phi_{ijkl})$	U(NB)	U(total)	Ref.
trans-*RR*-[Co(2,2,2-tet)(NH$_3$)$_2$]$^{3+}$	1.38	7.81	4.53	6.37	20.09	61
trans-meso-[Co(2,2,2-tet)(NH$_3$)$_2$]$^{3+}$	1.42	5.03	6.29	6.52	19.25	61
s-*cis*-[Co(2,2,2-tet)(Gly)$_2$]$^{2+}$	nr [b]	nr	nr	nr	5.5	64
uns-*cis*-[Co(2,2,2-tet)(Gly)$_2$]$^{2+}$	0.39	3.43	5.11	−3.75	5.2	64
trans-*RR*-[Co(2,2,3-tet)Cl$_2$]$^+$	1.86	4.75	9.75	7.29	23.65	31
trans-*RS*-[Co(2,2,3-tet)Cl$_2$]$^+$	1.79	4.79	9.80	7.02	23.40	31
uns-*cis*-*RS*-[Co(2,2,3-tet)Cl$_2$]$^+$	1.88	6.21	10.03	7.46	25.58	31
uns-*cis*-*SS*-[Co(2,2,2-tet)Cl$_2$]$^+$	1.82	7.37	9.99	6.25	25.43	31
uns-*cis*-*RS*-[Co(2,2,2-tet)Cl$_2$]$^+$	1.62	4.25	9.76	6.07	21.71	31
uns-*cis*-*RR*-[Co(2,2,2-tet)Cl$_2$]$^+$	1.59	6.60	9.90	5.81	23.89	31
trans-*SS*-[Co(3,2′,3-tet)Cl$_2$]$^+$	2.33	6.02	1.09	1.79	11.23	66
trans-*RR*-[Co(3,2′,3-tet)Cl$_2$]$^+$	2.45	10.27	1.43	4.88	19.03	66
trans-*SR*-[Co(3,2′,3-tet)Cl$_2$]$^+$	2.46	7.03	1.80	3.42	14.71	66
trans-*RS*-[Co(3,2′,3-tet)Cl$_2$]$^+$	2.61	7.94	1.31	3.79	15.65	66
uns-*cis*-[Co(R-3,2′,3-tet)Cl$_2$]$^+$	2.76	7.84	0.59	3.31	14.50	66
uns-*cis*-[Co(R-3,2′,3-tet)Cl$_2$]$^+$	2.79	7.70	0.76	3.66	14.91	66
s-*cis*-[Co(R-3,2′,3-tet)Cl$_2$]$^+$	3.11	8.82	0.69	4.42	17.04	66
trans-*RSSR*-[Co(3′,2,3′-tet)Cl$_2$]$^+$	2.79	6.45	0.94	7.73	18.31	68
trans-*RSSS*-[Co(3′,2,3′-tet)Cl$_2$]$^+$	3.02	8.23	0.86	8.49	20.60	68
trans-*SSSS*-[Co(3′,2,3′-tet)Cl$_2$]$^+$	3.03	9.12	0.84	8.26	21.26	68
s-*cis*-[Co(S-picpn)Cl$_2$]$^+$	0.31	6.71	3.29	0.85	11.16	22
s-*cis*-[Co(S-picpn)Cl$_2$]$^+$	0.25	6.55	1.80	0.34	8.84	22
uns-*cis*-[Co(S-picpn)Cl$_2$]$^+$	0.27	6.99	1.94	0.99	10.19	22
uns-*cis*-[Co(S-picpn)Cl$_2$]$^+$	0.23	6.12	2.24	0.64	9.24	22
uns-*cis*-[Co(S-picpn)Cl$_2$]$^+$	0.23	7.87	3.50	1.50	13.11	22
uns-*cis*-[Co(S-picpn)Cl$_2$]$^+$	0.26	10.41	2.60	1.27	14.55	22

[a] Abbreviations: 2,2,2-tet = 1,8-diamino-3,6-diazaoctane; 2,2,3-tet = 1,9-diamino-3,6-diazanonane; 3,2′,3-tet = 1,10-diamino-4,7-diaza-5-methyldecane; 3′,2,3′-tet = 1,10-diamino-4,7-diaza-2,9-dimethyldecane; and S-picpn = *N*,*N*′-bis(2-picolyl)-1,2(*S*)-propanediamine.

[b] Not reported.

Molecular mechanics calculations have been applied to triethylenetetraamine complexes of the form [Co(trien)AA]$^{2+}$ (AA = proline [62], *N*-methylalanine [63] and glycine [64,65]). The results of these calculations, together with calculations for some other tetraamine complexes, are shown in Table 10. All of the calculated structures are highly strained, due in part to the three interconnected chelate rings. Several of the isomers have also been studied crystallographically, with the crystallographic and calculated structures in remarkable agreement.

The calculated structures of uns-*cis*$_2$-(*RRS*)-[Co(trien)pro]$^{2+}$ [62] (Fig. 6) and uns-*cis*$_2$-(*SSS*)-[Co(trien)pro]$^{2+}$ are both in excellent agreement with the

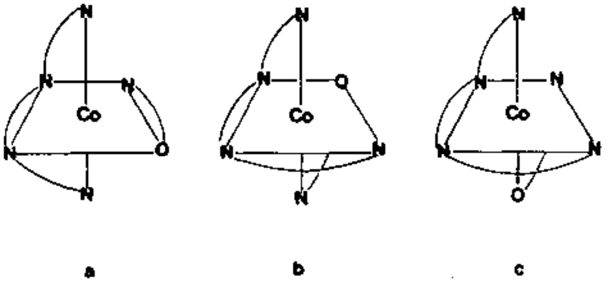

Fig. 6. Geometrical isomers of mixed ligand complexes with flexible tetraamine ligand and an amino acid. (a) *s-cis*; (b) uns-cis_1; (c) uns-cis_2.

observed structures. The Co–N–C angles in the coordinated proline are larger than expected; these increased angles serve to reduce the non-bonded H–H repulsions between the proline and trien ligands. The other bond angles around the Co(III) ion are smaller than 90° because of the small bite angles of five-membered chelate rings. The valence angles of the nitrogen and carbon atoms in the chelate rings are found to be within 1° of the normal 109.5°. The energy difference between the two complexes which have been isolated is 1.6 kcal mol^{-1}. The other two possible isomers for *S*-proline, which were not found in the reaction mixture, were calculated bearing significantly higher strain energies.

Four of the isomers of uns-cis_2-[Co(trien)(*N*-methyl-alanine)]$^{3+}$ [63] have been characterized either crystallographically or in solution. All of the isomers exhibit significant steric crowding by the *N*-methyl group; equilibrium studies indicate approximately equal stabilities for the *RRS*(*S*) and *RSS*(*S*) isomers. However, strain energy calculations indicate a 3.2 kcal mol^{-1} higher strain energy for the *RRS*(*S*) isomer. The inconsistency might be a result of the different entropies of formation for the two complexes.

Ten different isomers (of 12 possible) of [Co(trien)gly]$^{2+}$ [64,65] are known. Strain energy minimization calculations on these isomers (shown in Table 11) indicate that the low-energy isomer is consistent with the observed ring conformations. One of the major causes of strain in these complexes is the non-bonded interaction between the glycine nitrogen and the methylene protons of the "planar" and "apical" rings of trien. The apical ring is better able, however, to dissipate these repulsions through distortions in the ring torsions and valence angles. Minor differences between the calculated and observed structures were ascribed to hydrogen bonding in the crystal lattice.

(b) Other flexible linear tetraamines

Strain energy minimization calculations have been successful in determining the structure of Co(III) complexes with a variety of linear tetraamines.

TABLE 11

Calculated strain energies for some isomeric (glycinato) (triethylenetetraamine)cobalt(III) complexes

Complex	Ring conformation	$U(R_{ij})$	$U(\theta_{ijk})$	$U(\phi_{ijkl})$	U(NB)	U(total)	Ref.
s-*cis*(*RR*)	δ,λ,δ	nr [a]	nr	nr	nr	7.1	64
s-*cis*(*RR*)	λ,λ,δ	nr	nr	nr	nr	7.4	64
s-*cis*(*RR*)	δ,λ,λ	nr	nr	nr	nr	8.3	64
s-*cis*(*RR*)	δ,δ,δ	nr	nr	nr	nr	5.5	64
uns-cis_1(*RR*)	δ,δ,λ	0.5	3.9	5.7	−3.1	7.0	65
uns-cis_1(*RR*)	λ,δ,λ	nr	nr	nr	nr	9.2	64
uns-cis_1(*RR*)	δ,λ,δ	0.5	4.4	6.2	−3.3	7.8	65
uns-cis_1(*RR*)	λ,λ,δ	nr	nr	nr	nr	9.3	64
uns-cis_2(*RR*)	δ,δ,λ	0.39	3.43	5.11	−3.75	5.2	64
uns-cis_2(*RR*)	λ,δ,λ	0.39	3.76	6.79	−3.49	7.5	64
uns-cis_2(*RR*)	δ,λ,δ	0.66	5.07	5.88	−2.59	9.0	64
uns-cis_2(*RR*)	λ,λ,δ	0.57	5.46	5.83	−2.56	9.3	64

[a] Not reported.

Calculations performed on cobalt complexes with 4,7-diaza-5(*R*)-methyl-1,10-decanediamine [66] compare the relative stabilities of different configurations of complexes with the same ligand. This series of calculations predicted the smallest strain energies for the *trans* complexes in complete agreement with experimental results. Uns-*cis* complexes are predicted to have the lower strain energy among the two possible *cis* isomers by about 3 kcal mol^{-1}. The calculations indicate the low-energy isomer should have both six-membered chelate rings in the chair conformation and the substituted five-membered ring in the gauche conformation. These strain energy minimization calculations were later confirmed independently by X-ray crystallography [67]. In Table 12, the calculated and observed bond distances and angles are compared.

Conformational analyses of complexes with the unsymmetrical tetraamine, 1,9-diamino-3,6-diazanonane [31], were used to support spectroscopic studies of the stereochemistry of the uns-*cis* complexes. The stereochemical assignment, based on proton NMR and later confirmed by ^{13}C NMR [32], was somewhat unexpected, with the terminal five-membered chelate ring perpendicular to the plane defined by the cobalt ion and the two secondary amine nitrogens (Fig. 7). The large energy difference between this conformation and the next lower in energy suggests this will be the only observed isomer [31].

Energy minimization calculations on the isomers of 1,10-diamino-4,7-diaza-2,9-dimethyldecane complexes of cobalt(III) [68] have demonstrated the

TABLE 12

Comparison of calculated and observed bond distances and angles for geometric isomers of cobalt(III) complexes with 1,10-diamino-4,7-diazadecane

Distance or angle	*trans*-$[Co(3,2,3\text{-tet})Cl_2]^+$		uns-*cis*-$[Co(3,2,3\text{-tet})L_2]^+$	
	X-ray [a]	Calc. [b]	X-ray [a]	Calc. [b]
Co–N(1)	1.991	2.06	1.964	2.07
Co–N(2)	1.977	2.05	1.967	2.06
Co–N(3)	1.985	2.06	1.962	2.05
Co–N(4)	1.984	2.06	1.956	2.06
N–C	1.489	1.49	1.478	1.49
C–C	1.510	1.55	1.501	1.55
C–C	1.515	1.55	1.505	1.55
C–N	1.483	1.49	1.472	1.50
N–C	1.482	1.49	1.492	1.49
C–C	1.512	1.55	1.493	1.55
C–N	1.495	1.49	1.479	1.49
N–C	1.479	1.49	1.507	1.50
C–C	1.508	1.55	1.510	1.55
C–C	1.510	1.55	1.484	1.55
C–N	1.481	1.49	1.500	1.49
N–Co–N	92.4	91.14	89.7	86.31
N–Co–N	86.6	86.33	93.1	86.22
N–Co–N	91.1	92.85	90.6	88.72
Co–N–C	120.2	120.9	120.3	121.0
N–C–C	111.5	112.1	112.0	113.0
C–C–C	113.7	111.1	112.7	112.0
C–C–N	112.0	111.7	112.9	114.7
C–N–Co		119.9	118.5	118.3
N–C–C	107.1	108.8	108.1	107.8
C–C–N	107.3	107.5	107.0	108.9
C–N–Co	107.3	106.1	109.0	106.0
Co–N–C		118.5	118.0	120.7
N–C–C	112.7	112.1	112.4	112.6
C–C–C	113.5	111.6	113.5	111.3
C–C–N	112.1	111.8	112.4	111.5
C–N–Co	119.7	120.4	117.9	120.4

[a] Ref. 67. [b] Ref. 66.

importance of two independent chiral centers. The complex with an axial methyl group is at higher energy, but not sufficiently high to cause a shift to the skew-boat ring conformation. The calculated energy difference of 2.95 kcal mol^{-1} is sufficient to predict the observed stability order.

Energy minimization calculations performed on a series of optically active cobalt(III) tetraamine complexes have led to the conclusion that the stereo-

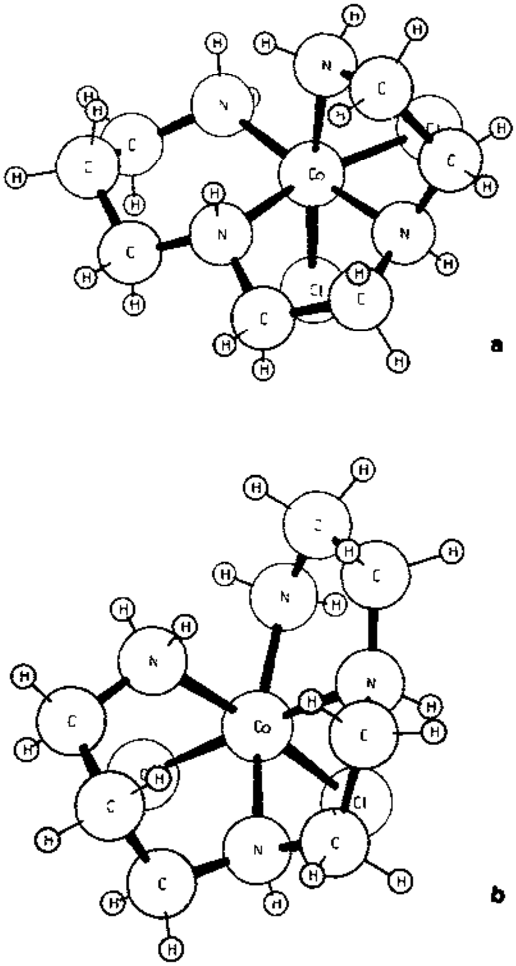

Fig. 7. Geometrical isomerism of complexes with the unsymmetrical ligand 1,9-diamino-3,6-diazanonane (2,2,3-tet). (a) uns-*cis* 2,2,3 (the five-membered chelate ring is displaced from the plane of the cobalt ion and the remaining nitrogen donors); (b) uns-*cis* 2,2,3 (the six-membered chelate ring is so displaced).

selectivity of the chelation of *N*-methyl amino acids should be much greater than that of the unsubstituted amino acids [69]. The increased selectivity arises from the greater difference in the strain energies caused primarily by interactions between the methyl group and several of the amine protons of the chelate ring.

(c) Tris(aminoethyl)amine [tren]

Structures for the two isomers of $[Co(tren)(NH_3)Cl]^{2+}$ (Fig. 8) have been

TABLE 13

Calculated energies for some tris(2-aminoethyl)amine and *N*-methyl-tris-(2-aminoethyl)aminecobalt(III) complexes

Complex [a]	$U(R_{ij})$	$U(\theta_{ijk})$	$U(\phi_{ijkl})$	U(NB)	U(total)	Ref.
trans-$[Co(tren)(NH_3)Cl]^{2+}$	0.91	3.20	5.93	0.67	10.71	70
cis-$[Co(tren)(NH_3)Cl]^{2+}$	0.79	2.70	5.84	0.59	9.93	70
cis-$[Co(tren)(gly)]^{2+}$	1.0	3.40	6.50	5.00	16.0	71
trans-$[Co(tren)(gly)]^{2+}$	1.5	3.30	7.20	6.70	18.8	71
anti-p(S)-$[Co(Metren)(NH_3)Cl]^{2+}$	1.28	4.33	5.91	1.78	13.30	72
anti-p(R)-$[Co(Metren)(NH_3)Cl]^{2+}$	1.28	4.44	5.78	1.90	13.25	72
syn-p(S)-$[Co(Metren)(NH_3)Cl]^{2+}$	1.32	3.72	5.98	1.90	12.92	72
syn-p(R)-$[Co(Metren)(NH_3)Cl]^{2+}$	1.29	3.73	6.01	1.89	12.92	72
S(S)-$[Co(Metren)(NH_3)Cl]^{2+}$	1.25	4.14	5.66	1.60	12.65	72
S(R)-$[Co(Metren)(NH_3)Cl]^{2+}$	1.24	4.36	5.89	1.60	13.09	72

[a] See Figs. 8 and 9 for designation of isomers.

determined experimentally and calculated [70] (the calculated energies are shown in Table 13). These structures agree on the details of the ring conformations; the energy difference is too small (0.8 kcal mol^{-1}), however, to permit reasonable predictions on the relative stabilities of the complexes. The greater energy in the isomer with the NH_3 *cis* to the tertiary nitrogen is a result of valence angle deformations caused by the interference of the amine protons with the two perpendicular chelate rings.

Calculations based on the structures of the two isomers of $[Co(tren)Gly]^{2+}$ indicate a much larger strain energy difference, though probably for similar reasons [71] (Table 13). The calculated energy difference of 2.8 kcal mol^{-1} is consistent with the observed isomer ratio. In this case the flattening of the chelate rings is also responsible for a small increase in energy in isomer (a) (Figs. 8 and 9). The largest increase is, again, a result of the interaction of

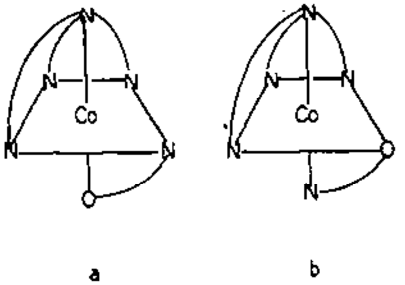

Fig. 8. Geometrical isomerism of mixed ligand complexes with tris (2-aminoethyl)amine and amino acids. (a) *cis*; (b) *trans*.

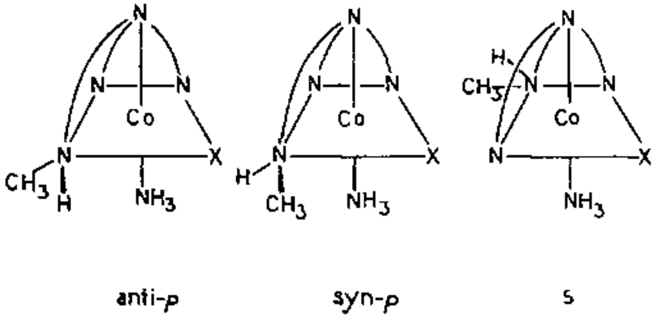

Fig. 9. Geometrical isomerism of complexes with 1-amino-3-(2-aminoethyl)-3,6-diazaheptane (*N*-methyltren).

the glycine N–H protons with the perpendicular chelate rings in the more-strained complex.

Conformational analysis of (*N*-methyltren)cobalt(III) complexes (Fig. 9) indicates that all six possible stereoisomers have similar strain energies (a range of 0.7 kcal mol^{-1} is observed) [72] (Table 13). The calculated structures of these complexes are in agreement with the experimentally determined structures; however, significant differences were noted in the Co–Cl and some Co–N bond lengths. The similar strain energies of the different isomers led to an incorrect energy ordering of the isomers. This study suggests that small differences in strain energy are often not significant.

(d) Rigid tetraamine ligands

The study of the cobalt(III) complexes with the ligand *N,N'*-bis(picolyl)-1,2(*S*)-propanediamine illustrated the use of the program to determine isomers for inflexible ring systems [22]. In the compounds studied the torsion angle strain and the valence angle deformations were found to be the primary sources of strain energy. The energies of the isomers showed that the release of strain is not responsible for the facile isomerization reaction. Calculations for related amino acid complexes [73] indicate that an optical purity of 60–80% for mixed-ligand complexes would be predicted based on strain energy alone.

(e) Macrocyclic ligands

A variety of different macrocyclic complexes of cobalt(III) have been studied by Hung and Busch [74]. In their study the log of the aquation rate constant was found to vary linearly with the strain energy of the complex

(Fig. 10). This correlation suggests a significant release of strain in the postulated five-coordinate intermediate. The study also suggests the influence of strain energy in the chloride dissociation rate, which is the rate determining step of the reaction. The strain energy of the macrocyclic complexes was found to increase with increasing distance between the donors.

Intramolecular strain energies for an homologous series of copper(II)

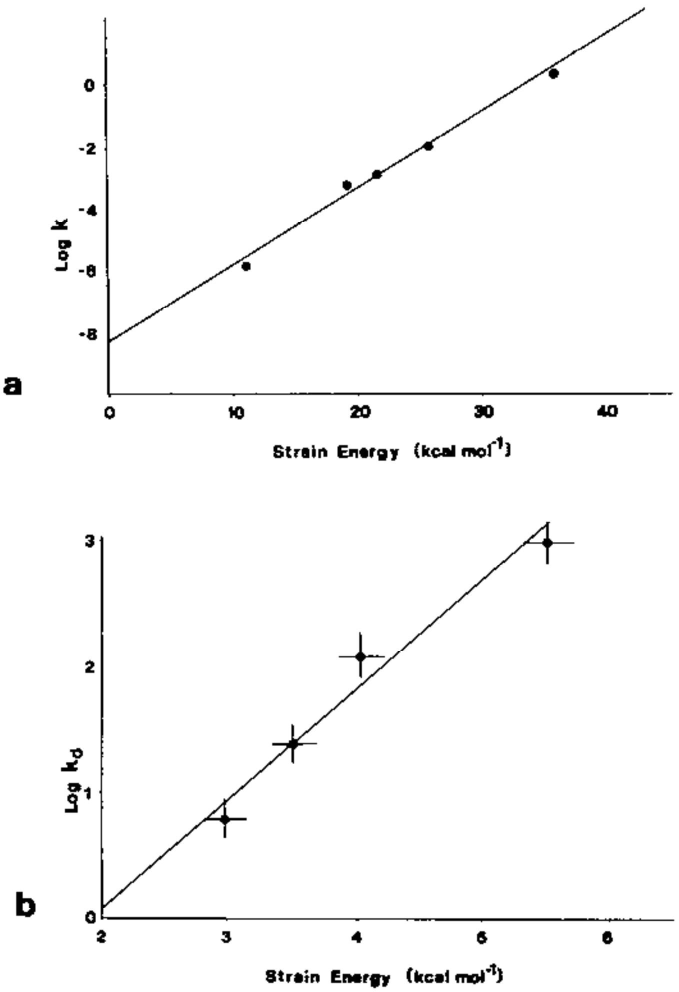

Fig. 10. Correlation of calculated ground state intramolecular strain energies with dissociation rate constants. (a) [Co(macrocycleN$_4$)Cl$_2$]$^+$ → [Co(macrocycleN$_4$)Cl]$^{2+}$ + Cl$^+$; (b) [Cu(macrocycleS$_4$)]$^{2+}$ → macrocycle + Cu^{2+} (see text).

polythiaether macrocycle complexes (Table 14) have been calculated [75] and compared with experimentally determined structures [76] stability constants, dissociation rates, and free energies of formation [77]. For the complexes with the tetrathia macrocycles, 1,4,7,10-tetrathiacyclododecane ([12]-ane-S_4), 1,4,7,10-tetrathiacyclotridecane ([13]-ane-S_4), 1,4,8,11-tetrathiacyclotetradecane ([14]-ane-S_4), 1,4,8,12-tetrathiacyclopentadecane ([15]-ane-S_4), and 1,5,9,13-tetrathiacyclohexadecane ([16]-ane-S_4), stability constants and dissociation rate constants decrease linearly with increasing intramolecular strain. The free energy of formation within this series is inversely proportional to intramolecular strain yielding a "strain-free" free energy of formation of -8.65 (0.66) kcal mol^{-1} for tetrathiaether macrocycle complexes of copper(II). The anomalous behavior of the pentathiaether ligand, 1,4,7,10,13-pentathiacyclopentadecane ([15]-ane-S_5), was ascribed to entropic terms. The unexpectedly high stability constant and low dissociation rate of $[Cu([12]\text{-ane-}S_4)]^{2+}$ was ascribed to structures in solution which have lower intramolecular strain than has the solid state structure.

These studies are particularly interesting because they compare the strain energies of complexes within homologous series, rather than among conformations of a single compound. Such calculations necessarily use different numbers of atoms and interactions in the force field model. It is interesting to note that strain energy does not increase monotonically as the number of atoms or interactions increases (i.e., in these examples, the effects of methylene groups are not simply additive). The validity of calculations which make such comparisons must rest on the correlations between these calculations and observable chemical phenomena.

TABLE 14

Calculated intramolecular strain energies for some polythiaether macrocycle copper(II) complexes

Complex	$U(R_{ij})$	$U(\theta_{ijk})$	$U(\phi_{ijkl})$	U(NB)	U(total)[a]	$\log(K_f)$[b]	$\log(k_d)$[b]
$Cu([12]\text{-ane}S_4)^{2+}$	0.277	3.436	3.305	-3.327	3.690	3.39	0.41
$Cu([13]\text{-ane}S_4)^{2+}$	2.279	5.537	1.540	-5.865	3.491	3.44	1.43
$Cu([14]\text{-ane}S_4)^{2+}$	2.093	5.003	1.375	-5.481	2.989	4.33	0.78
$Cu([15]\text{-ane}S_4)^{2+}$	0.846	5.010	2.921	-4.653	4.104	3.18	2.20
$Cu([16]\text{-ane}S_4)^{2+}$	0.910	5.431	3.742	-4.532	5.524	2.20	3.03
$Cu([15]\text{-ane}S_5)^{2+}$	0.617	7.736	5.791	-2.904	11.240	4.18	1.69

[a] Interaction constants from Tables 1–4. [b] D.B. Rorabacher, M.J. Martin, M.J. Koenigbauer, M. Malik, R.R. Schroeder, J.F. Endicott and L.A. Ochrymowycz, in K. Karlin and J. Zubieta (Eds.), Biochemical and Inorganic Perspectives in Copper Coordination Chemistry, Adenine Press, Guilderland, NY, 1983.

(iv) Complexes with pentadentate and hexadentate ligands

Energy minimization studies of cobalt complexes with tetraethylenepentaamine [21] and pentaethylenehexaamine [78] have been attempted. The crystal structure of the tetraethylenepentaamine complex showed some intermolecular interactions resulting in the deformation of one chelate ring [21]. Despite this deformation, both the calculated and observed structures had similar features. The structure observed in the crystal was found to be about 2.5 kcal mol^{-1} higher in strain than the minimum-energy conformation. The hexaamine structural isomers were shown to be very close in energy, even so the major isomer observed is the lowest in strain energy [78].

C. EMERGING APPLICATIONS

Boyd's strain energy minimization technique provides an option for the calculation of the vibrational frequencies of a strain energy minimized structure. Combined with computer-simulated isotopic substitution, this option permits either rapid and accurate assignment of vibrational spectra, or detailed refinement of interaction constants from a comparison of experimental and calculated vibrational frequencies.

The ability of strain energy minimization calculations to predict the energies of the different stereoisomers of metal complexes (primarily cobalt amine complexes) has been established. Some studies indicate the importance of strain energy in thermodynamic properties of metal complexes. Future advances are likely to be made by the application of this type of calculation to other metal complexes and other donors.

Some recent data has indicated that strain energy minimization calculations will be useful in the prediction of dynamic processes. Preliminary reports suggest application of molecular mechanics calculations to the estimation of Frank–Condon barriers to electron transfer reactions [79]. The calculations can give an estimate of the transition state structure, and an improved estimate to the energy of the transition state.

Recent data also indicates strain energy minimization calculations may predict the stereochemical course of some reactions [80]. The calculation allows the structure to relax, after the dissociation of one ligand, to the "strain free" state and a prediction of the stereochemical course of the reaction can be made from the geometry of the intermediate.

These new applications to dynamic processes should lead to important new uses for molecular mechanics calculations in coordination chemistry.

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