Society, is gratefully acknowledged. Also, we are grateful to Dr. William E. Hatfield for the use of some of his research facilities and to Mr. William B. Skelton and Leonard A. Zyzyck for some of the spectra.

Contribution from the Department of Physical and Inorganic Chemistry,
The University of Adelaide, Adelaide, South Australia 5001, Australia

Symmetry-Constrained Force Fields in the Prediction of Molecular Geometries of Metal Complexes. I

MARK DWYER, RODNEY J. GEUE, and MICHAEL R. SNOW*

Received December 8, 1972

The theoretical and practical aspects of symmetry-dependent strain energy refinement of the structures of metal complexes are reported. Use of this procedure reduces computation per cycle to approximately one-fifth of that required by independent refinement and in addition requires substantially less core storage. The fixing of individual cartesian atomic coordinates in both independent and symmetry-dependent refinements is discussed and in particular it is shown how a symmetry trap may be avoided. For the symmetrical facial bis(diethylenetriamine)cobalt(III) ion, results of independent and symmetry-dependent refinements constrained to two symmetry point groups are presented and compared with X-ray crystal data. Calculations on the lowest strain energy isomer of carbonatobis(trimethylenediamine)cobalt(III) are also cited.

Introduction

Recent publications[1] have reported the calculation of thermodynamic parameters and molecular geometries for metal complexes. The potential energy of a molecule with N atoms is represented by the summation

$$U_{\text{total}} = \Sigma U_{\text{B}} + \Sigma U_{\text{NB}} + \Sigma U_{\theta} + \Sigma U_{\phi}$$

where U_{B}, U_{NB}, U_{θ}, and U_{ϕ} are functions describing the potential energy of bond length deformations, nonbonded contacts, valence angle deformations, and bond torsion, respectively. The mathematical forms of these functions are adequately described, if not justified, elsewhere.[2] U_{total} is measured from an arbitrary zero level, which has significance only for the comparison of two stereoisomers. For an individual molecule, U_{total} represents the potential energy difference between the predicted structure and a configuration of that molecule, strainless with respect to the above four modes. Although in most instances this strainless, zero-level configuration cannot have physical reality, comparisons of potential energies with experimental data are valid for configurational isomers but specifically exclude comparisons of linkage isomers. The molecular geometry defined by minimum U_{total} and the value of U_{total} itself have been correlated with experimental data.[1]

In many of the molecules studied by us, one common observation was prevalent, namely, that the molecular symmetry, intrinsic in a molecular model, was preserved almost precisely in the calculated conformation of the strained molecule. We wish to report the theoretical and practical considerations of an extension of the present refinement procedure,[3] applicable to metal complexes of any point group. This extension not only allows the investigation of a metal complex constrained to its symmetric configuration(s) but also constitutes a significant reduction in computing time and memory requirements.

Theory and Discussion

Minimization on the energy surface is implemented by curve fitting to the function U_{total} as described by Boyd.[4] The mathematical procedure for nonrefinement of symmetry-dependent atoms is described in the Appendix.

In addition to this, we have found it necessary to incorporate a routine to fix discrete coordinates of any atom in the input list. The coordinates to be constrained are dictated by the particular symmetry conditions and disposition of atoms relative to symmetry elements. This option must be included to prevent spurious results and is discussed below.

A cycle of symmetry-dependent refinement involves modulation of the asymmetric atom positions in the force field imposed by the entire molecule. The pertinent symmetry operations are then used to reconstruct the molecule from the refined asymmetric atoms, whence the modified force field is generated and the cycle iterated. This mode is continued to convergence. The rate of convergence may depend on the size of coordinate shifts however, and a damping function should be employed to maximize this rate. However, the use of a fixed damping factor to achieve the maximum convergence rate within a particular potential energy well is unsatisfactory, since the damping is applied without reference to the size of coordinate shifts. In generating the damping factor, it has been assumed the direction of the calculated translation vector ($\Delta \mathbf{X}_i^{\alpha}$) is correct but that the magnitude is overestimated. This stems from the fact that the direction is correct at the point of fit or of extrapolation to zero magnitude and leads to a linear dependence between the corrected translation vector and the calculated one. Furthermore, it was decided that the larger elements of the translation vector should have more control over the magnitude of the estimated damping factor. In practice, calculated elements may range from 10^{-4} to 2 Å and unless stringent discrimination is required, a function dependent on the sum of the squares of the vector elements will principally reflect the larger ones. A function of the form

$$\lambda = 1/(1 + (\text{SHAPE})\sum_{i=1}^{N}\sum_{\alpha=1}^{3}(\Delta X_i^{\alpha})^2)$$

is found to be adequate in reducing the possibilities of oscilla-

---

(1) (a) D. A. Buckingham, I. E. Maxwell, A. M. Sargeson, and M. R. Snow, *J. Amer. Chem. Soc.*, **92**, 3617 (1970); (b) D. A. Buckingham, I. E. Maxwell, and A. M. Sargeson, *Inorg. Chem.*, **9**, 2663 (1970); (c) M. R. Snow, *J. Amer. Chem. Soc.*, **92**, 2610 (1970).

(2) J. William, P. Stang and P. Von Schleyer, *Annu. Rev. Phys. Chem.*, **19**, 531 (1968), and references therein.

(3) Program adapted from that of R. Boyd, *J. Chem. Phys.*, **49**, 2574 (1968); modified by M. R. Snow and I. E. Maxwell (1968) and M. Dwyer (1970).

(4) R. Boyd, *J. Chem. Phys.*, **49**, 2574 (1968).

tion and escape to remote sections of the surface. At the same time smooth refinements undergo rapid convergence. The shape of the damping function curve is determined by the parameter SHAPE which is preset to obtain the maximum convergence rate consistent with the above conditions. We have found values of 1-2 satisfactory for many refinements.

The major time and core size differences between the dependent and full refinement techniques are connected with the size of the coefficient matrix. Core size varies as the square and the equation solution time varies as the approximate cube of the linear dimension of the matrix. In addition, the matrix generation time is roughly proportional to the square of this dimension.

In both dependent and independent refinement techniques, we fix certain discrete coordinates for different reasons.

First, we consider an independent refinement ideally involving simultaneous adjustment of all atoms. The potential energy of the system is initially a function of internal coordinates only. Hence the system, which is exempt from external forces, will not translate or rotate. This may occur to some extent in an individual cycle as a result of inexact fitting of the power series to the energy surface, but permanent rotation and translation are absent by definition of the system's potential function. However if this system is converted to cartesian coordinates and no restrictions are applied, the potential energy becomes a mathematical function of $3N$ independent cartesian coordinates. Minimization of this function with respect to these $3N$ coordinates will result in $3N$ linear equations, the solutions of which are obtained with no restrictions on the spatial disposition of the molecule. Hence while the true potential function provides no physical incentive for the molecule to change position as a whole, the modified function with no restraints on translation and rotation does not contain this information. The solutions to the $3N$ equations will then generally contain rotational and translational components. These may be reduced to a negligible extent by the fixing of six cartesian coordinates in the molecule, since all atoms or groups of atoms are connected in some way to the atoms on which the coordinates are constrained.

We now describe the consequence of fixing any cartesian coordinate in this system and the way in which we exploit this to activate a break from symmetry in independent refinement.

The potential energy is a function only of internal coordinates and hence of normal vibrational coordinates, since the two sets span the same vector space. Thus if these coordinates are expanded in a series of cartesian coordinates, the fixing of any cartesian coordinate constrains the variance of the normal or internal coordinate of which it is part. We here interpret variance to mean the ability of the system to change under the influence of the force field imposed by the potential function. Specifically, if any cartesian coordinate is constrained, the component of motion of the appropriate internal coordinate in that direction is impeded, even though the motion in the directions of all other cartesian coordinates is free. This means that some internal coordinates are not given the driving force calculated from the gradient of the potential function. Although the driving force in an individual cycle is incorrect, the iterative nature of the refinement allows the system to rectify itself continually, so that the result at convergence is correct. However, the very fact that a component of the motivation is deleted in a given cycle may mean that an initially symmetric molecule is no longer symmetric after that cycle. In this way, cartesian coordinate fixing may be employed to allow a symmetric starting molecule to break from the symmetry trap imposed by the symmetric force field. Now for an independent refinement, six coordinates must be fixed to prevent the molecule as a whole from translating or rotating in a zero external force field. Since a total of only six coordinates are to be restricted, they must be chosen in such a manner as to allow the system to escape from the symmetric force field if present. The essential condition is that a component of motion incompatible with the molecular symmetry must be allowed. In principle, six coordinates satisfying this condition and including at least one component along each coordinate axis may be fixed on any atoms in the molecule to break the symmetry. Physical restrictions may narrow the choice however. Thus interconnectivity of the force field may not be sufficient, for an atom on which a coordinate is fixed, to break the symmetry in a remote part of the molecule. Nevertheless it has been found that the method is relatively insensitive to these effects unless there is absolutely no connectivity or coordinate shift. An important consideration which must be observed in choosing coordinates to fix is that there are no constraints on the magnitudes of internal coordinates in the course of the refinement. It must be ensured that the internal coordinates involving a fixed cartesian coordinate are free to adopt chemically reasonable values. It is not necessary, however, that a coordinate system be chosen[1a] such that the fixed coordinates have zero values.

The justification and reasons for coordinate fixing in symmetry-dependent refinement follow a different rationale: for atoms not resident on symmetry elements, a specific cycle involves refinement of atoms in the input asymmetric unit, while the symmetry-generated atoms are fixed. Since the force field is symmetric, the driving force on each symmetry-equivalent atom is the same. Hence rebuilding of the molecule by symmetry from the refined asymmetric atoms results in precisely the same structure as would have been obtained by an independent refinement with no coordinates fixed. The imposed symmetry introduces the only restriction on the molecule, and it is this that allows us to implement the above atom-fixing procedure. The symmetry refinement also allows atoms on symmetry elements to be constrained to move in accord with the symmetry. This means that these atoms are defined to move along a line or a plane, or if on a center of symmetry, not at all. Once again there is no constraint on internal coordinate variance other than the symmetry condition. When the symmetry element is a line or plane, the only resultant force component on an atom resident on this element is along the line or plane. Thus forcing the atom to remain on the symmetry element in no way affects the variance of the internal coordinates. Similarly, for an atom on a center of symmetry in a centrosymmetric force field, the total resultant force is zero and this atom may be fixed, in a symmetry-dependent refinement. It is advisable to adhere to the foregoing procedure for the following reasons. During a cycle of refinement, the symmetry-dependent sections of the molecule are kept fixed, while the input-independent section is allowed to refine (see the Appendix). Thus the symmetry information is not contained in the coefficients of refining atom shifts during an individual cycle. Consequently the atom initially on a symmetry element, which is fixed in space, may not lie on that element after a given cycle. An oscillatory motion may then result near convergence.

Although this refinement method may follow a different path to one in which the symmetry information is contained in the coefficients, no difficulty has been found in locating the same potential well located by a symmetry-independent

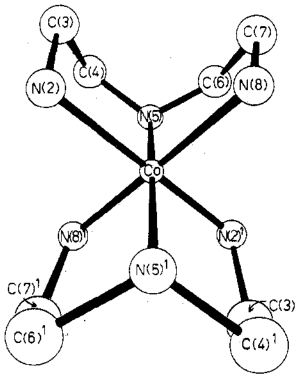

Figure 1. The symmetrical facial $[Co(dien)_2]^{3+}$ ion.

refinement. This has been shown by executing one or two cycles of independent refinement from the convergence point of the dependent refinement. The results are identical with those of a complete independent refinement of the same molecule. The advantage of this method of symmetry-dependent refinement lies in the small number of coordinate shift coefficients to be calculated. For a problem involving 30-40 atoms, these require more calculation time than the solution of the linear equations. For problems involving smaller numbers of refining atoms, much larger fractions of the cycle times are concerned with calculating coefficients. Many extra coefficient calculations are required in a symmetry-dependent refinement in which the symmetry information is contained in the refining atom coefficients. This severely offsets the time advantage in solving the equations, which was gained by reducing the number of refining variables, and may even result in a larger cycle time than for an independent refinement of the same molecule. Despite the fact that our method may follow a different path and require more cycles to converge, the cycle times are so dramatically reduced that the total refinement time for a symmetry-dependent refinement is far less than that for the corresponding independent refinement. In addition, unless perhaps the potential well is very poorly defined, the correct one is found as discussed above and usually only requires one or two cycles of independent refinement to locate the independent minimum.

Results

The results from symmetry-dependent and -independent refinements demonstrate that the output atomic coordinates define molecules which contain no structural abnormalities, are equivalent in structure, symmetry, and strain energy, and differ marginally from the experimentally determined structure.

The model structure for the symmetrical facial[5] $[Co(dien)_2]^{3+}$ ion (dien ≡ diethylenetriamine), Figure 1, was computed from standard bond lengths and angles with estimated torsion angles for atoms Co, N(2), C(3), C(4), N(5), C(6), C(7), and N(8). Hydrogen atom positions were calculated assuming tetrahedral bonding. Refinements were initiated from a trial structure possessing exact C_i and approximate C_{2h} symmetry. The C_i symmetry was retained in the independent refinement. For the C_{2h}-dependent refinement the ion was defined by the atoms Co, N(2), C(3), C(4), and N(5) and attendant hydrogen atoms. The Co atom was fixed on the center of symmetry and N(5) and its hydrogen were constrained to lie on the mirror plane. The ion was defined by Co, N(2), C(3), C(4), N(5), C(6), C(7), and N(8) and attendant hydrogen atoms for the C_i refinement with Co fixed on the center of symmetry.

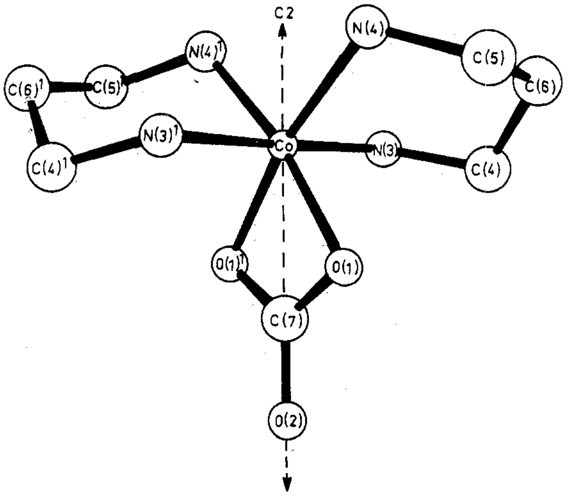

Figure 2. The $[Co(tn)_2CO_3]^+$ ion.

Table I. Molecular Geometry of $[Co(dien)_2]^{3+}$

	Symmetry independent	C_i dependent	C_{2h} dependent	Crystal
	Bond Lengths, Å			
Co-N(2)	1.959 (1.959)[a]	1.959[b]	1.959[b]	1.97 (1)[c]
Co-N(5)	1.935 (1.935)	1.935	1.935	1.95 (1)
Co-N(8)	1.958 (1.959)	1.958	1.959	1.97 (1)
N(2)-C(3)	1.495 (1.495)	1.495	1.497	1.47 (2)
C(3)-C(4)	1.506 (1.506)	1.506	1.506	1.54 (2)
C(4)-N(5)	1.501 (1.501)	1.501	1.500	1.49 (2)
N(5)-C(6)	1.500 (1.501)	1.500	1.500	1.52 (2)
C(6)-C(7)	1.507 (1.507)	1.507	1.506	1.48 (2)
C(7)-N(8)	1.499 (1.499)	1.499	1.497	1.49 (2)
	Valence Angles, Deg			
N(2)-Co-N(5)	88.38 (88.39)	88.40	88.29	86.6 (5)
N(2)-Co-N(8)	90.50 (90.49)	90.50	90.50	89.5 (5)
N(5)-Co-N(8)	88.03 (88.04)	88.05	88.29	87.2 (5)
Co-N(2)-C(3)	108.44 (108.42)	108.48	109.44	111.6 (10)
N(2)-C(3)-C(4)	108.85 (108.84)	108.89	109.42	107.7 (12)
C(3)-C(4)-N(5)	109.84 (109.84)	109.85	110.00	109.9 (12)
C(4)-N(5)-C(6)	113.73 (113.73)	113.73	113.79	116.0 (12)
N(5)-C(6)-C(7)	110.09 (110.09)	110.09	110.00	109.4 (12)
C(6)-C(7)-N(8)	109.89 (109.89)	109.87	109.42	109.5 (12)
C(7)-N(8)-Co	110.12 (110.12)	110.09	109.44	109.7 (10)
	Torsion Angles, Deg			
Co-N(2)-C(3)-C(4)	33.85 (33.88)	33.54	27.61	30.8 (10)
Co-N(5)-C(4)-C(3)	32.95 (32.94)	33.12	36.10	38.2 (10)
Co-N(5)-C(6)-C(7)	38.91 (38.92)	38.75	36.10	40.0 (10)
N(5)-C(6)-C(7)-N(8)	39.50 (39.48)	39.61	41.98	44.0 (13)
C(6)-C(7)-N(8)-Co	21.14 (21.10)	21.47	27.61	27.2 (10)
N(2)-C(3)-C(4)-N(5)	44.13 (44.14)	44.03	41.98	45.5 (13)

[a] Figures in parentheses refer to structural elements related by preservation of the unimposed C_i symmetry. [b] Symmetry-related features are not tabulated for the dependent refinements, since the symmetry is exact by the definition of dependent refinement. [c] Estimated standard deviations in parentheses.

For the $[Co(tn)_2CO_3]^+$ ion (tn = trimethylenediamine), Figure 2, initial coordinates were obtained from the crystallographic coordinates of the "B ring" and part of the carbonate chelate of the $[Co(tn)_2CO_3]ClO_4$ structure.[6] Coordinates were orthogonalized, with the cobalt ion centered on the origin and the axes reoriented such that the *z* axis was collinear with the carbonyl of the carbonate chelate. The second tn chelate and the remainder of the carbonate chelate

---

(5) Nomenclature as in F. R. Keene and G. H. Searle, *Inorg. Chem.*, 11, 148 (1972).

(6) R. J. Geue and M. R. Snow, *J. Chem. Soc. A*, 2981 (1971).

Table II. Molecular Geometry from $[Co(tn)_2CO_3]^+$ C_2 Refinement

Bond lengths	Value, Å	Bond angles	Value, deg	Torsion angles	Value, deg
Co-N(3)	1.984	N(3)-Co-N(4)	87.52	Co-N(3)-C(4)-C(6)	67.49
Co-N(4)	1.972	N(3)-Co-O(1)	94.38	N(3)-C(4)-C(6)-C(5)	63.24
Co-O(1)	1.882	N(4)-Co-O(1)	97.47	C(4)-C(6)-C(5)-N(4)	63.86
N(3)-C(4)	1.497	Co-N(3)-C(4)	113.70	C(6)-C(5)-N(4)-Co	68.27
C(4)-C(6)	1.510	N(3)-C(4)-C(6)	111.44		
C(6)-C(5)	1.510	C(4)-C(6)-C(5)	112.33		
C(5)-N(4)	1.498	C(6)-C(5)-N(4)	111.87		
O(1)-C(7)	1.313	C(5)-N(4)-Co	113.22		
		Co-O(1)-C(7)	84.95		
		O(1)-C(7)-O(2)	121.47		

atom positions were obtained by a C_2 operation about the z axis.

For reasons discussed above, the atomic coordinates x, y, z of Co, y, z of N(3), and z of C(4) of the $[Co(tn)_2CO_3]^+$ structure and x, y, z of Co, y, z of N(2), and z of N(5) of the $[Co(dien)_2]^{3+}$ structure were fixed. However for symmetry-dependent refinement, the atomic coordinates x, y, z of Co and x, y of both O(2) and C(7) of the $[Co(tn)_2CO_3]^+$ structure and x, y, z of Co in the $[Co(dien)_2]^{3+}$ structure were fixed. The $[Co(dien)_2]^{3+}$ structure required 15 cycles of independent refinement and 25 sec/cycle using 126160 words but 12 cycles for refinement constrained by a center of symmetry and 5 sec/cycle using 62060 words.[7,8]

For the $[Co(tn)_2CO_3]^+$ ion, 16 cycles of independent refinement took 16 sec/cycle using 100161 words, but 32 cycles for symmetry-dependent refinement took 3 sec/cycle using 60320 words.

The molecular geometries obtained from these refinements are presented in Tables I and II. Table I also shows the results of a crystal structure analysis[9] of $[Co(dien)_2]Br_3$. Table III contains the final atomic coordinates. The most sensitive structural details of these molecules are the bond torsion angles. This sensitivity is undoubtedly due to the weak force constant of ∿3 kcal/mol[1a] for a 60° deformation from the staggered conformation. The agreement between dependent and independent refinements is excellent.

The $[Co(tn)_2CO_3]^+$ isomer examined had an inherent C_2 axis collinear with the carbonyl bond of the coordinated carbonate ion. The tn rings have the chair conformation and this isomer had been previously found[4] to have the lowest strain energy of three possible conformational isomers. The C_2 symmetry was enforced for the dependent refinement of the structure using the basis atoms Co, O(1), C(7), O(2), N(3), C(4), C(6), C(5), and N(4) and attendant hydrogen atoms. Comparison of the internal dimensions of the output molecules confirms the maintenance of both the C_2 axis and the chair conformation of the tn chelates. All differences in bond lengths and angles between symmetry-dependent and -independent refinements were less than 0.001 Å and 0.01°, respectively. As a consequence the contributions from each type term and the total strain energy (Table IV) are practically identical. This isomer of $[Co(tn)_2CO_3]^+$ has not so far been isolated.

Table III. Final Positional Parameters (Orthogonal, Å)

$[Co(dien)_2]^{3+}$

	C_i refinement			C_{2h} refinement		
Atoms	x	y	z	x	y	z
Co	0.000	0.000	0.000	0.000	0.000	0.000
N(2)	1.959	0.000	0.001	1.940	−0.025	0.273
N(5)	0.053	−0.454	1.880	−0.213	−0.202	1.912
C(3)	2.432	−0.028	1.419	2.237	−0.026	1.740
C(4)	1.460	−0.831	2.242	1.094	−0.668	2.482
C(6)	−0.472	0.725	2.645	−0.684	1.108	2.471
C(7)	0.014	2.006	2.018	−0.039	2.247	1.727
N(8)	−0.017	1.886	0.524	−0.029	1.942	0.261
N(2)H(1)	2.308	0.810	−0.449	2.354	0.772	−0.144
N(2)H(2)	2.324	−0.787	−0.476	2.350	−0.823	−0.145
C(3)H(1)	2.528	0.954	1.800	2.407	0.957	2.092
C(3)H(2)	3.389	−0.486	1.465	3.123	−0.585	1.919
C(4)H(1)	1.611	−1.864	2.049	1.166	−1.723	2.390
C(4)H(2)	1.639	−0.661	3.274	1.158	−0.426	3.513
N(5)H(1)	−0.540	−1.232	2.041	−0.903	−0.892	2.088
C(6)H(1)	−0.154	0.680	3.657	−0.448	1.178	3.504
C(6)H(2)	−1.533	0.709	2.639	−1.738	1.178	2.374
C(7)H(1)	0.989	2.239	2.361	0.943	2.420	2.083
C(7)H(2)	−0.624	2.800	2.320	−0.599	2.134	1.898
N(8)H(1)	0.774	2.346	0.145	0.770	2.354	−0.154
N(8)H(2)	−0.821	2.343	0.171	−0.825	2.349	−0.163

$[Co(tn)_2CO_3]^+$

	C_2 refinement				C_2 refinement		
Atoms	x	y	z	Atoms	x	y	z
Co	0.000	0.000	0.000	C(6)H(1)	1.992	2.679	1.724
N(3)	−0.006	1.982	0.045	C(6)H(2)	3.243	2.812	0.557
C(4)	1.320	2.596	−0.280	C(5)H(1)	2.980	0.449	−0.002
C(6)	2.341	2.305	0.794	C(5)H(2)	3.405	0.695	1.640
C(5)	2.631	0.828	0.925	N(4)H(1)	1.709	−0.859	1.599
N(4)	1.423	0.059	1.364	N(4)H(2)	1.055	0.477	2.183
N(3)H(1)	−0.681	2.312	−0.602	O(1)	1.115	−0.106	−1.512
N(3)H(2)	−0.280	2.294	0.944	C(7)	0.000	0.000	−2.198
C(4)H(1)	1.669	2.237	−1.214	O(2)	0.000	0.000	−3.438
C(4)H(2)	1.203	3.649	−0.363				

The dien ligand may be considered as a pair of ethylenediamine molecules fused at a common nitrogen atom. For the independent refinement of the $[Co(dien)_2]^{3+}$ ion, examination of the torsion angles about corresponding bonds, for example about C(3)-C(4) and C(6)-C(7), demonstrates the absence of mirror symmetry within the dien ligands. Thus this calculated $[Co(dien)_2]^{3+}$ ion conforms to C_i rather than to C_{2h} symmetry. The ion in $[Co(dien)_2]Br_3$ conforms more closely to C_{2h} symmetry.[7] Table IV shows that the strain energy difference between the C_i and C_{2h} models is small (0.4 kcal/mol) and resides almost entirely in the nonbonded energy term. This in turn results from the direct opposition of hydrogen atoms across the mirror plane in the C_{2h} model. Underlying this symmetry distinction is the difference between the environment of the calculated *ion* and experimentally determined *molecule*. The environment about the $[Co(dien)_2]^{3+}$ ion in the crystal of $[Co(dien)_2]Br_3$, while itself conforming to C_i symmetry, allows for a hydrogen bond with the protons of the secondary dien nitrogen atoms. This hydrogen bond seems most likely to be responsible for the

---

(7) All computations were carried out using a CDC 6400 computer, operating under SCOPE 3.2. In all instances, program MOL2 was loaded in binary from magnetic tape and execution times quoted are exclusive of compilation and peripheral processor but include loader times. Times and core storage extents are reported in decimal seconds and octal words, respectively. The sole routine utilized from the CDC systems library (ENCODE/DECODE) or an equivalent is generally available on computer installations.

(8) Subsequent developments, including triangularization of the coefficient matrix, have reduced core requirements to 57304 words for independent refinement of the $[Co(dien)_2]^{3+}$ ion.

(9) M. Kobayashi, F. Marumo, and Y. Saito, *Acta Crystallogr., Sect. B*, **28**, 470 (1972).

Table IV. Final Energy Terms (kcal/mol)

	$[Co(dien)_2]^{3+}$			$[Co(tn)_2CO_3]^+$	
	Independent	C_i dependent	C_{2h} dependent	Independent	C_2 dependent
ΣU_B	0.94	0.93	0.95	2.00	1.99
ΣU_{NB}	6.12	6.10	6.68	7.48	7.49
ΣU_θ	2.24	2.23	2.19	2.52	2.52
ΣU_ϕ	7.87	7.87	7.87	0.34	0.34
U_{total}	17.17	17.13	17.61	12.34	12.34

minor twisting of the dien rings from the calculated structure. In other respects the calculated and experimental data (within experimental error) do not differ; for example the calculated reduction of the Co-N(5) bond length relative to those of the Co-N(2) and Co-N(8) bonds and the expansion of the angle C(4)-N(5)-C(6) considerably above the tetrahedral value are observed.

Appendix

A quadratic Taylor series expansion about a trial geometry (r°_{ij}, θ°_{ijk}, ϕ°_{ijkl}, $r^\circ_{ij\mathrm{NB}}$) effectively conforms a parabolic function to the energy surface in this region. A mode of expression[4] is

$$U = U(r^\circ_{ij}, \theta^\circ_{ijk}, \phi^\circ_{ijkl}, r^\circ_{ij\mathrm{NB}}) + \sum_{\substack{ij \\ i<j}} \left(\frac{\partial U_\mathrm{B}}{\partial r_{ij}}\right)_{r^\circ_{ij}} \Delta r_{ij} +$$

$$^1\!/_2 \sum_{\substack{ij \\ i<j}} \left(\frac{\partial^2 U_\mathrm{B}}{\partial r_{ij}^2}\right)_{r^\circ_{ij}} \Delta r_{ij}^2$$

plus similar expressions for $\Delta\theta_{ijk}$, $\Delta\phi_{ijkl}$, and $\Delta r_{ij\mathrm{NB}}$ variables. Here r_{ij} symbolizes a bond distance, θ_{ijk} a bond angle, ϕ_{ijkl} a torsional angle, and $r_{ij\mathrm{NB}}$ a nonbonded distance. Cross terms in the expansion are zero since they are neglected in the energy function, which at this point is considered as an independent function of all interaction coordinates. Application of the minimum condition is facilitated by transformation to independent cartesian coordinates by expansion about the trial cartesian geometry;[4] *e.g.*

$$r_{ij} = r^\circ_{ij} + \sum_{\alpha=1}^{3} I_r^\alpha \Delta X_i^\alpha + \sum_{\alpha=1}^{3} J_r^\alpha \Delta X_j^\alpha +$$

$$^1\!/_2 \sum_{\alpha,\beta=1}^{3} \sum_{\substack{P=I,J \\ Q=I,J}} (P^\alpha Q^\beta)_r \Delta X_P^\alpha \Delta X_Q^\beta$$

where

$$I_r^\alpha = (\partial r_{ij}/\partial X_i^\alpha)_{X_i^{\alpha\circ}}$$

$$J_r^\alpha = (\partial r_{ij}/\partial X_j^\alpha)_{X_j^{\alpha\circ}}$$

$$I^\alpha J^\beta = (\partial^2 r_{ij}/\partial X_i^\alpha \partial X_j^\beta)_{X_i^{\alpha\circ} X_j^{\beta\circ}}$$

The minimum condition is then applied whereby $\partial U/\partial X_i^\alpha = 0$ for $\alpha = 1, 2, 3$ and $i = 1, \ldots, N$ atoms. $3N$ linear equations in the cartesian shifts are obtained from which the translation vector ΔX_i^α ($\alpha = 1, 2, 3$; $i = 1, \ldots, N$) is determined by a modified Gauss elimination procedure. In matrix notation $\mathbf{A}\Delta\mathbf{X} = \mathbf{Y}$ where $\mathbf{A} = (a_{ij})$ is the matrix of shift coefficients and $\mathbf{Y} = (y_i)$ is the column vector of noncoefficient parameters.

If there is a nonrefining atom j, the Taylor series expansion of the energy does not depend on the coordinates ΔX_j^α ($\alpha = 1, 2, 3$). All terms containing ΔX_j^α ($\alpha = 1, 2, 3$) vanish and all other terms remain the same. Thus the partial derivatives $\partial U/\partial X_j^\alpha$ ($\alpha = 1, 2, 3$) are not defined since ΔX_j^α is not a variable, and there are no terms containing ΔX_j^α ($\alpha = 1, 2, 3$) in any of the other partial derivatives. The new coefficient matrix **A** is therefore obtained by removing all rows and columns associated with the coordinates of the nonrefining atom j from the original matrix. The new column vector **Y** is obtained by removing the elements Y_j^α ($\alpha = 1, 2, 3$) determined by partial differentiation of U with respect to the coordinates of j. Hence the positions of elements removed from **Y** correspond to the positions of the rows removed from **A**. Both independent refinement and our method of symmetry-dependent refinement involve nonrefining coordinates and atoms, but the matrix generation procedure differs for the two cases.

In symmetry-dependent refinement, the input atom list only contains those atoms in the asymmetric unit of the molecule. The asymmetric unit is defined with respect to the symmetry to be retained in the molecule during refinement and not necessarily the full inherent symmetry. The remaining atoms of the molecule are then symmetry generated and added to the end of the input atoms list. These atoms are not refined and the rows and columns of **A** and **Y** corresponding to them are not calculated. In an individual cycle of refinement, the input asymmetric atoms are refined, and all interactions of these with the nonrefining symmetry-generated atoms are included in the calculation of contributions to **A** and **Y**. Thus the asymmetric unit is refined in the fixed field of the symmetry generated atoms. The fixed atoms are then symmetry regenerated from the refining set after the cycle. This results in overcalculation of shift contributions from interactions between refining and nonrefining atoms. However, as stated in the Discussion, no difficulty has been found in locating the minimum of the correct potential well, even in molecules with many strong interactions between refining and nonrefining symmetry-dependent parts.

For the nonrefinement of coordinates within a refining set of atoms, as in independent refinement to prevent translation and rotation, or for atoms lying on symmetry elements in dependent refinement, a different method is used. Here the total **A** matrix and **Y** vector for the refining set of atoms are generated. The superfluous rows and columns corresponding to the nonrefining atom coordinates are then removed by a routine which compresses the **A** and **Y** matrices.