The electronic spectra of Mn^{2+} and Mn^{3+} complexes differed significantly from each other. The divalent complex decomposed in the light path of the spectrometer, but for fast scans reflectance spectra showing only weak absorptions expected for high-spin d^5 were obtained. The Mn^{3+} system showed a rich spectrum with intense absorptions enumerated in Table IV. In a recent detailed study of the spectra[38] of octahedral Mn^{3+} complexes, the unusual low-energy bands for these systems were attributed to transitions between the components of a Jahn–Teller split ^5E_g ground state. Transitions to a similarly split $^5T_{2g}$ excited state were also observed. In the present investigation, the near-infrared transitions are observed at energies even lower than those of the studies just cited. This is attributed to the weak-field nature of terpyO_3 combined with a more highly distorted arrangement of the six oxygens in $Mn(terpyO_3)_2(ClO_4)_3$.

Conclusions

The results of this investigation show that terpyO_3 readily forms a series of pseudooctahedral and tetrahedral complexes. The best interpretation of the data indicates that terpyO_3 acts as a tridentate ligand although the evidence for this in some of the complexes, particularly $Cu(terpyO_3)Cl_2$ and $Ni(terpyO_3)_2(ClO_4)_2 \cdot 2H_2O$, is not as conclusive. It is interesting that there is little tendency for the formation of five-coordinate complexes while the "parent" ligand terpyridine forms an extensive series of such complexes with the first transition series metals. The lack of planarity of terpyO_3 and its acting as a base for a "C_{3v}" pyramid may favor four-coordination. Solid-state packing effects for such a bulky ligand are also probably important but difficult to estimate in their effect on stereochemistry.

Acknowledgment.—The authors wish to thank the National Science Foundation for support of this work.

(38) T. S. Davis, J. P. Fackler, and M. J. Weeks, *Inorg. Chem.*, **7**, 1994 (1968).

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Conformational Analysis of Coordination Compounds. III. Bis- and Tris-Bidentate Complexes Containing Five-Membered Diamine Chelate Rings

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Previously published experimental data concerning the energy differences between the various configurations of $Co(en)_3^{3+}$ have been reinterpreted, and it has been shown that there is very little energy difference between the D(δδδ) {=L(λλλ)} and D(δδλ) {=L(λλδ)} configurations and that both these structures are considerably preferred over the other configurations. Estimation of these energies based on conformational energies arising from van der Waals, torsional, and angle-bending energy terms has shown that the energy differences are very sensitive to the type of van der Waals equation used. The more established equations for this type of system due to Hill and Mason and Kreevoy were found to be completely inadequate in accounting for the observed energy differences. Although the Bartell nonbonded interaction equation was able to account satisfactorily for the difference in energy between the D(δδδ) and D(λλλ) configurations, it erroneously predicted that the D(δδλ) configuration was significantly more stable than D(δδδ). Empirical equations of the Hill type were developed to account for the energy differences, and these were tested by applying them to the estimation of the energy difference between the axial and equatorial orientations of the methyl group in methylcyclohexane. An energy of the right order was obtained. For *cis*-bis-ethylenediamine complexes, the *a priori* calculations showed that there is very little energy difference between the possible configurations, and, for the *trans* isomer, the chiral and *meso* configurations were found to have identical energies.

The preferred configurations for tris-ethylenediamine and related complexes have been the subject of a number of recent investigations. Corey and Bailar estimated from conformational energy calculations that, for the D distribution of chelate rings, the energy of the possible configurations increased in the order (δδδ) < (δδλ) < (δλλ) < (λλλ) with an energy difference between the D(δδδ) and D(λλλ) configurations of 1.8 kcal mol^{-1}.[1] This was in reasonably good agreement with an experimentally determined value of 1.6 kcal mol^{-1}.[2] Prior to 1968, all X-ray evidence supported this preference for the D(δδδ) or L(λλλ) configurations, as no other configuration had been found in the crystalline state.[3,4] However, more recently, Ibers and his coworkers have reported examples of each of the other configurations in pentacyanonickelate(II) and hexacyanocobaltate(III) salts of tris(ethylenediamine)chromium(III).[5]

cis-Bis-ethylenediamine complexes, in which the remaining octahedral positions are occupied by uniden-

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(1) E. J. Corey and J. C. Bailar, *J. Am. Chem. Soc.*, **81**, 2620 (1959).

(2) F. P. Dwyer, T. E. MacDermott, and A. M. Sargeson, *ibid.*, **85**, 2913 (1963).

(3) M. A. Porai-Koshits, *Russ. J. Inorg. Chem.*, **13**, 644 (1968).

(4) Y. Saito, *Pure Appl. Chem.*, **17**, 21 (1968).

(5) K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *Inorg. Chem.*, **7**, 842, 1362 (1968); K. N. Raymond and J. A. Ibers, *ibid.*, **7**, 2333 (1968).

tates or by planar, or nearly planar, chelates are found to exhibit all three possible configurations in the crystalline state.[3] For example, *d*-$[\mathrm{Co(en)_2(CN)_2}]\mathrm{Cl\cdot H_2O}$ has the D(λλ) configuration,[6] in contrast to D-$[\mathrm{Co(en)_2(L\text{-}glu)}]\mathrm{ClO_4}$, which has the D(δδ),[7] and $\mathrm{Ni(en)_2(NCS)Cl}$,[3] which has the δλ configuration. This is consistent with the small experimentally determined energy differences between D(λλ) and L(λλ) for $\mathrm{Co((}R\mathrm{)\text{-}pn)_2ox^+}$.[8]

Corey and Bailar have also calculated the energy differences between the chiral and *meso* forms of *trans*-bis-ethylenediamine complexes.[1] They found the chiral isomers were preferred by about 1 kcal $\mathrm{mol^{-1}}$. This preference is not shown in the crystalline state as all complexes of this type so far studied by X-ray diffraction have been found to be centrosymmetric.[3,4] Saito has suggested that the δλ form must be favored by specific intermolecular forces in the crystalline state,[4] and Porai-Koshits has proposed that the normal close-packing requirements for molecules in solids are responsible for the preference for the *meso* configuration.[3]

In a previous paper from this laboratory, the conformations of ethylenediamine and substituted ethylenediamine chelate rings were investigated by detailed *a priori* calculations of conformational energies for complexes containing one chelate ring.[9] The techniques developed in that paper are applied here to the bis- and tris-diamine complexes. As so much experimental information is available for these systems, it was hoped that this investigation would enable a choice to be made between the various types of van der Waals energy equations. In fact, the calculated energy difference between the D(δδδ) and D(λλλ) configurations for the tris complexes proved to be very sensitive to the type of van der Waals equation, and it was possible to show that the results obtained with low- and high-energy equations, which have previously been applied to metal complex systems, are inconsistent with the experimental data. An empirical van der Waals equation was derived to account for the experimental energy differences between the four types of configuration and was tested by applying it to the estimation of the energy difference between axial and equatorial orientations of the methyl group in methylcyclohexane.

Experimental Configurational Energy Differences for Tris Complexes

Dwyer and his coworkers have determined the equilibrium constant for the system

$$\mathrm{D\text{-}Co((}R\mathrm{)\text{-}pn)_3^{3+}} \rightleftharpoons \mathrm{L\text{-}Co((}R\mathrm{)\text{-}pn)_3^{3+}}$$

to be 14.6 by equilibrating $\mathrm{Co((}R\mathrm{)\text{-}pn)_3^{3+}}$ on charcoal and separating the two diastereoisomers quantitatively.[2,10] As the chelated (*R*)-propylenediamine prefers almost exclusively the λ conformation with the methyl group equatorial,[11] this corresponds to an energy difference between the D(λλλ) and L(λλλ) configurations of 1.6 kcal $\mathrm{mol^{-1}}$. Dwyer and his group[2] have also determined the energy differences between the four types of configurations by equilibrating a mixture of cobalt, ethylenediamine, and (*R*)-propylenediamine and determining the ratios of the concentrations of the D and L isomers of the "mixed" complexes $\mathrm{Co(en)_2((}R\mathrm{)\text{-}pn)^{3+}}$ and $\mathrm{Co(en)((}R\mathrm{)\text{-}pn)_2^{3+}}$. They assumed that, for the D configuration, the ethylenediamine chelate ring adopted the δ conformation and that for the L, it adopted the λ conformation, whereas the (*R*)-propylenediamine chelate ring retained its λ conformation irrespectively of the configuration. Based on this assumption, they calculated the following relative energies for the D(δδδ), D(δδλ), D(δλλ), and D(λλλ) configurations: 0, 0.45, 1.2, and 1.6 kcal $\mathrm{mol^{-1}}$. MacDermott has subsequently reported that one of the fractions isolated was incorrectly identified,[12] and, using the data he provided and the assumption of the previous paper,[2] the relative energies become 0, 0.65, 0.8, and 1.6 kcal $\mathrm{mol^{-1}}$.

However, their basic assumption that the conformation of the ethylenediamine is completely fixed by the configuration is far too restrictive. They in fact presupposed that there would be a large energy difference between the various configurations. The ethylenediamine can adopt both conformations, the relative concentrations of each being determined by the energy differences between the four types of configuration. It was also assumed that, in the λ conformation with the methyl group equatorial, (*R*)-propylenediamine is energetically equivalent to ethylenediamine with the same conformation. Thus, at equilibrium, allowing

$$\frac{[\mathrm{L}(\lambda\lambda\delta)]}{[\mathrm{L}(\lambda\lambda\lambda)]} = a, \qquad \frac{[\mathrm{L}(\lambda\delta\delta)]}{[\mathrm{L}(\lambda\lambda\lambda)]} = b, \qquad \frac{[\mathrm{L}(\delta\delta\delta)]}{[\mathrm{L}(\lambda\lambda\lambda)]} = c$$

and as D(δδλ) = L(λλδ), D(δλλ) = L(λδδ), and D(λλλ) = L(δδδ), then

$$\frac{[\mathrm{L\text{-}Co(en)_2((}R\mathrm{)\text{-}pn)^{3+}}]}{[\mathrm{D\text{-}Co(en)_2((}R\mathrm{)\text{-}pn)^{3+}}]} = \frac{[\mathrm{L}(\lambda\lambda\lambda)] + [\mathrm{L}(\delta\lambda\lambda)] + [\mathrm{L}(\delta\delta\lambda)]}{[\mathrm{D}(\lambda\lambda\lambda)] + [\mathrm{D}(\delta\lambda\lambda)] + [\mathrm{D}(\delta\delta\lambda)]} = \frac{1 + a + b}{c + b + a} = \frac{12.6}{7.1} \qquad (1)$$

and

$$\frac{[\mathrm{L\text{-}Co(en)(}R\mathrm{\text{-}pn)_2^{3+}}]}{[\mathrm{D\text{-}Co(en)(}R\mathrm{\text{-}pn)_2^{3+}}]} = \frac{[\mathrm{L}(\lambda\lambda\lambda)] + [\mathrm{L}(\delta\lambda\lambda)]}{[\mathrm{D}(\lambda\lambda\lambda)] + [\mathrm{D}(\delta\lambda\lambda)]} = \frac{1 + a}{c + b} = \frac{35.7}{7.7} \qquad (2)$$

As c has been determined to be $^1/_{14.6}$,[2] eq 1 and 2 can be solved to give $a = 0.81$ and $b = 0.32$. These values give rise to the following relative energies (kcal $\mathrm{mol^{-1}}$) for the above four configurations: D(δδδ), 0; D(δδλ), 0.1; D(δλλ), 0.7; D(λλλ), 1.6. These values are very similar to those determined from a study of the tris cobalt(III) complexes prepared from a 2:3:3 mixture of cobalt and (*R*)- and (*S*)-propylenediamine under equilibrium conditions: 0, 0, 0.52, and 1.6 kcal $\mathrm{mol^{-1}}$, re-

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[6] K. Matsumoto, Y. Kushi, S. Ooi, and H. Kuroya, *Bull. Chem. Soc. Jap.*, **40**, 2988 (1967).

[7] J. H. Dunlop, R. D. Gillard, N. C. Payne, and G. B. Robertson, *Chem. Commun.*, 874 (1966).

[8] F. P. Dwyer, T. E. MacDermott, and A. M. Sargeson, *J. Am. Chem. Soc.*, **85**, 661 (1963).

[9] J. R. Gollogly and C. J. Hawkins, *Inorg. Chem.*, **8**, 1168 (1969).

[10] F. P. Dwyer, F. L. Garvan, and A. Shulman, *J. Am. Chem. Soc.*, **81**, 290 (1959).

[11] The preference for the equatorial orientation should be in excess of 0.7 kcal $\mathrm{mol^{-1}}$ for each (*R*)-propylenediamine chelate in the tris complex.[9]

[12] T. E. MacDermott, *Chem. Commun.*, 223 (1968).

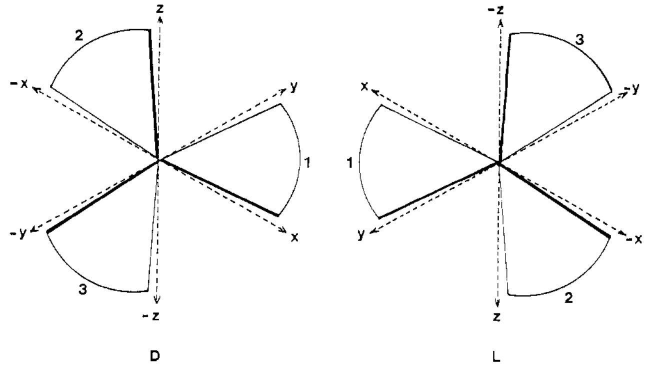

Figure 1.

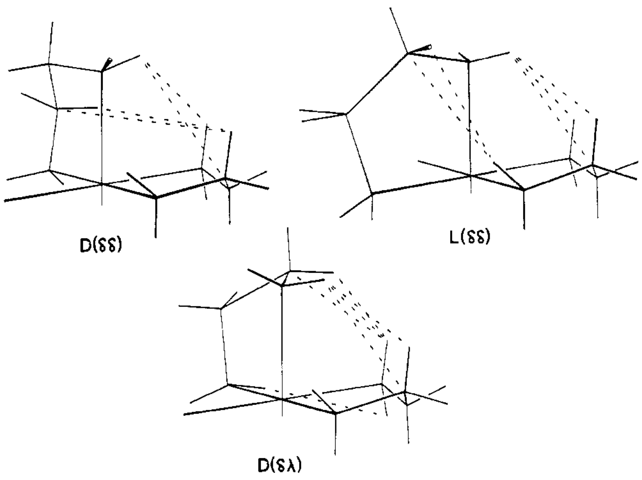

Figure 2.—*cis*-Bis-ethylenediamine interaction systems.

spectively.[13] It was claimed that the latter result was dependent not only on the configurational energy differences but also on energy terms that arose from a 1:3:3:1 probability ratio of forming the Co((*R*)-pn)$_3^{3+}$, Co((*R*)-pn)$_2$((*S*)-pn)$^{3+}$, Co((*R*)-pn)((*S*)-pn)$_2^{3+}$, and Co((*S*)-pn)$_3^{3+}$ complexes.[13] However, this ignored the fact that the species of the type Co((*R*)-pn)((*R*)-pn)((*S*)-pn)$^{3+}$, Co((*R*)-pn)((*S*)-pn)((*R*)-pn)$^{3+}$, and Co((*S*)-pn)((*R*)-pn)((*R*)-pn)$^{3+}$ are completely indistinguishable. When this is taken into account, it can be seen that the four complexes are formed with equal probability. When the cobalt:(*R*)-propylenediamine:(*S*)-propylenediamine ratio was changed to 1:2:1, the probability of forming the above four complexes would have been in the ratio of 3:2:2:3 according to the present statistical reasoning. This is consistent with the changes observed in the ratio of the concentrations of the complexes.

Geometrical Model

A convenient method for specifying the conformation of five-membered chelate rings has been discussed previously.[9] Under this model, the chelate ring is placed in a Cartesian coordinate system so that the coordinate bonds of the ring lie in the xy plane. For a constant set of ring bond lengths, the precise conformation of the ring can then be uniquely defined by the choice of $\angle$N(1)MN(2) ($=\alpha$), $\angle$MN(1)C(1) ($=\beta$), and z_1 and z_2, the z coordinates of the two carbon atoms. In these calculations, the position of the ring in the xy plane has been chosen so that the coordinate bonds make equal angles with the x and y axes, respectively (Figure 1). The coordinates of substituents to the ring may then be obtained by simple geometry using the appropriate set of substituent bond lengths and bond angles.

Once the coordinates of a chelate ring have been determined in this way, the ring may then be moved into other positions in the complex by suitable coordinate transformations. In octahedral tris complexes of bidentates, the chelate rings may be distributed around the threefold axis in either of two isomeric ways, which are designated D and L (Figure 1). The conformational energy of each of these isomers arises from the individual energies of each ring (the ring-strain energy) and from the interactions between three pairs of rings that are *cis* to each other, *i.e.*, (1,2), (2,3), and (3,1). In the cases where the three rings have the same chirality, symmetry requires that a threefold axis relates the positions of the atoms in these rings. Because of the symmetry of these complexes, their interaction systems are related in the following way

$$\mathrm{D}(\delta\delta\delta) = \mathrm{L}(\lambda\lambda\lambda) = 3\mathrm{D}(\delta\delta) \tag{3}$$

$$\mathrm{D}(\lambda\lambda\lambda) = \mathrm{L}(\delta\delta\delta) = 3\mathrm{L}(\delta\delta) \tag{4}$$

Consequently, for such complexes, it is only necessary to consider the interactions between one pair of rings (*e.g.*, 1 and 2) whose conformations are identical. It is sufficient to determine the coordinates of ring 1 in the normal way and then to generate the coordinates of ring 2 by the coordinate transformation appropriate to the symmetry of the complex.

In the tris complexes with mixed chiralities for the conformations, the threefold axis does not link the conformations of the three rings, and, as a result, the interacting pairs of rings are not all equivalent, and the conformations are not necessarily related by any simple symmetry relationships. However, in order to simplify the calculations, it has been assumed that the rings of opposite chirality are enantiomeric. With this condition, the interaction systems for the "mixed" complexes can be simplified to

$$\mathrm{D}(\delta\delta\lambda) = \mathrm{L}(\lambda\lambda\delta) = \mathrm{D}(\delta\delta) + 2\mathrm{D}(\delta\lambda) \tag{5}$$

$$\mathrm{D}(\delta\lambda\lambda) = \mathrm{L}(\delta\delta\lambda) = \mathrm{L}(\delta\delta) + 2\mathrm{L}(\delta\lambda) \tag{6}$$

$$\mathrm{D}(\delta\lambda) = \mathrm{L}(\delta\lambda) \tag{7}$$

To investigate the mixed *cis* interaction system, D($\delta\lambda$), with ring 1 having coordinates (x, y, z), the coordinates of ring 2 are generated by transforming the coordinates (x, y, $-z$) instead of (x, y, z). Once again the coordinates of only one ring are needed to define the whole system. The interaction systems are diagrammatically represented in Figure 2 showing the major nonbonded interactions.

For the *trans*-bis-ethylenediamine complexes, the rings were situated in the xy plane as discussed above, and the geometries of the two rings were varied independently.

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(13) F. P. Dwyer, A. M. Sargeson, and L. B. James, *J. Am. Chem. Soc.*, **86**, 590 (1964).

Energy Terms

The torsional and angle-bending equations used in this paper and the parameters with which they have been applied have been described previously.[9] As before, bond lengthening was considered to be too energetically unfavorable to be of any significance in these calculations.

The nonbonded interaction forces which determine the structure of molecules have the general property of being strongly repulsive at small interatomic distances, and either negligibly small or slightly attractive at large interatomic distances. Many attempts have been made to describe these interatomic interaction forces quantitatively. These range from purely theoretical approaches to empirical equations designed to fit various types of experimental data. As shown in Figure 3, the empirically derived equations for H···H interactions differ widely both in the shape of the repulsive part of the interaction curve and in the H–H distance at which the interactions become significantly repulsive. The wide range of equations arises both from the varying sources of experimental data and from the varying criteria applied to the empirical equations.

One physically observable quantity which has been commonly used in the choice of empirical equations is the closest distance of approach of atoms in crystals as determined by X-ray structural studies. The value of this parameter for two nonbonded hydrogen atoms has been estimated at approximately 2.4 Å.[14] In deriving interaction equations for H···H interactions, this parameter has sometimes been interpreted as the interatomic distance at which the interaction energy is at a minimum. Hill's equation is typical of those that satisfy this requirement.[15] However, it has been suggested that this parameter actually corresponds to a point at which the interactions begin to become significantly repulsive.[16] Bartell's equation is consistent with this.[17] In the region of 2.4 Å, the interaction energy predicted by Mason and Kreevoy[18] is far too high to account for the observed distances of closest approach. Although the Mason and Kreevoy equation has been used as a general nonbonded interaction equation by Corey and Bailar,[1] it was considered by its proponents to be effective only in the interaction region $r \leqslant 1.8$ Å. The C···H interaction equations of Hill and Bartell satisfy conditions which are analogous to those discussed for the H···H equations, the distance of closest approach in this case being 2.7 Å.[14] Only Hill has proposed an N···H van der Waals equation. However, the significance of any N···H interaction when using Bartell's equations has been gauged by applying Bartell's C···H potential function to the N···H interaction system. This would tend to overestimate the energy of interaction, but, even so, it was found for the present systems that the N···H interactions were insignificant.

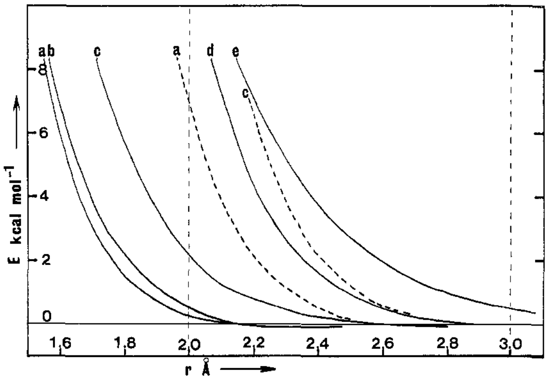

Figure 3.—Nonbonded interaction curves: (a) Hill;[15] (b) J. B. Hendrickson, *J. Am. Chem. Soc.*, **83**, 4537 (1961); (c) Bartell;[17] (d) Allinger and coworkers;[16] (e) Mason and Kreevoy.[18] A full line represents H···H interactions, and a broken line represents C···H interactions.

In the region of interest of this study, $2.0 \text{ Å} \leqslant r \leqslant 3.0$ Å, Hill's (a), Bartell's (c), and Mason and Kreevoy's (e) curves for the interactions are representative of low-, moderate-, and high-energy equations, respectively (Figure 3). The three have been applied here to the tris-ethylenediamine system to see which could account best for the experimental data.

Results

Calculations on the basis of the above geometrical model have been performed for $\alpha = \angle N(1)MN(2) = 86°$ and $\beta = \angle MN(1)C(1) = 109.5°$, these values being chosen on the basis of the results of a previous paper.[9] The ring has been varied symmetrically ($z_1 = -z_2$) by varying z_1 between 0.00 and +0.50 Å with increments of 0.05 Å. For nonsymmetric conformations (though still δ) z_1 has been held in turn at +0.20 and +0.00 Å and z_2 has been varied from 0.00 to −0.80 Å with increments of 0.10 Å.

The bond lengths and bond angles used to define the positions of substituents to the ring have been described previously, as have the constant bond lengths assumed for the ring itself.[9] The possibility of small distortions in α and β occurring to relieve unfavorable interactions has been considered. However, a brief investigation has shown that such distortions will not affect the general conclusions of this study.

Computer programs were used to calculate the geometry of the interaction systems, as well as the relevant interatomic distances.

Figure 4 shows the effect of varying chelate ring conformations on the van der Waals energy of the interaction systems, D($\delta\delta$) and L($\delta\delta$). When ω, the dihedral angle between the N(1)C(1)C(2) and N(2)-C(2)C(1) planes, is 0 and the chelate ring is completely flat, the interactions between the rings are identical for D and L configurations and are relatively small, although the rings, *per se*, are under great strain. As the puckering of the rings increases, the interactions in both isomers increase but at rather different rates. When ω is small, the interactions favor the L complex. As ω

[14] A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).

[15] T. L. Hill, *J. Chem. Phys.*, **16**, 399 (1948).

[16] N. L. Allinger, M. A. Miller, F. A. Van Catledge, and J. A. Hirsch, *J. Am. Chem. Soc.*, **89**, 4345 (1967).

[17] L. S. Bartell, *J. Chem. Phys.*, **32**, 827 (1960).

[18] E. A. Mason and M. M. Kreevoy, *J. Am. Chem. Soc.*, **77**, 5808 (1955).

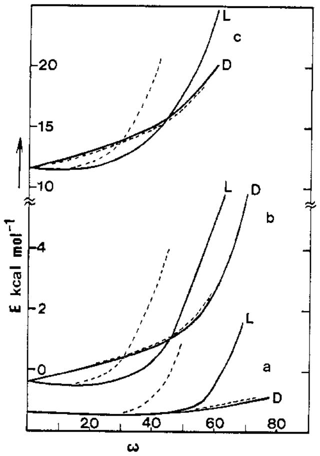

Figure 4.—Variation of E_v with change in chelate ring conformation for D($\delta\delta$) and L($\delta\delta$), using (a) Hill's, (b) Bartell's, and (c) Mason and Kreevoy's interaction equations: ——, $z_1 = -z_2$; – – –, $z_1 = 0.0$.

increases further and the ring becomes more puckered, the repulsive interactions in the L complex begin to increase more rapidly than in the D complex until, finally, the van der Waals interactions favor the D complex at a point where the ring is fairly highly staggered. The major contribution to the energy differences comes from the following interactions: for D, C(1)···H_{ax}–N(1)′, N(2)–H_{ax}···C(2)′; for L, C(1)···H_{eq}–N(2)′, N(1)–H_{eq}···C(2)′. The N···H interactions do not contribute significantly to either the total energy or the energy differences, but certain H···H interactions (see Figure 2) make relatively large contributions to the total interaction energy.

In the D form, the interactions are rather insensitive to whether the ring conformations are varied symmetrically or nonsymmetrically, the energy of interaction depending mainly on the degree of puckering. Only in the conformations with $z_1 = 0$ are the interactions significantly larger than those in the symmetrical conformations.

Graphs of the variation of the sum of van der Waals, torsional, and angle-bending energies with ring conformation are shown in Figure 5. The energy differences between the minimum-energy structures for the L($\delta\delta$) {= D($\lambda\lambda$)} and D($\delta\delta$) configurations were found to be (a) for Hill's equation, 0, (b) for Bartell's, +0.27 kcal mol^{-1}, and (c) for Mason and Kreevoy's, −0.8 kcal mol^{-1}.

Bartell's equation was then used to calculate the energy differences for the complete series of tris configurations including the mixed complexes D($\delta\delta\lambda$) and D($\delta\lambda\lambda$). In the mixed interaction system D($\delta\lambda$), the major contributions to the van der Waals interaction energy come from the H···H interactions, C(1)–H_{ax}···H_{ax}–N(1)′, N(2)–H_{ax}···H_{ax}–N(1)′, and N(2)–H_{ax}···H_{ax}–C(1)′, and the C···H interactions, C(1)···H_{ax}–N(1)′ and N(2)–H_{ax}···C(1)′. In this system the interaction energies for the symmetrical conformations were found to be similar to those in the D($\delta\delta$) system. However, when the rings assumed nonsymmetric conformations, both the H···H and C···H interaction energies were significantly reduced, leading to an energy preference for nonsymmetric conformations in this system.

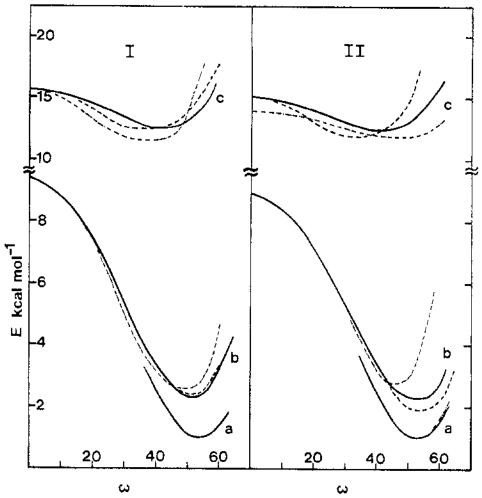

Figure 5.—Variation of total energy with change in chelate ring conformation for the D($\delta\delta$) (——), D($\delta\lambda$) (– – –), and L($\delta\delta$) (–·–·) interaction systems using (a) Hill's, (b) Bartell's, and (c) Mason and Kreevoy's interaction equations: I, symmetrical distortion with $z_1 = -z_2$; II, unsymmetrical distortion with $z_1 = 0.2$ Å.

The sum of the van der Waals, torsional, and angle-bending energies for D($\delta\lambda$) was calculated for each conformation of the range studied, as had been done for the D($\delta\delta$) and L($\delta\delta$) systems. To determine the relative energies of D($\delta\delta\delta$), D($\delta\delta\lambda$), D($\delta\lambda\lambda$), and D($\lambda\lambda\lambda$), the total energy curves for the appropriate bis interaction systems were summed according to eq 3–7, and each of the minimum energies was determined. These are collected in Table I.

Table I

Calculated Minimum Energies[a] for $M(en)_3$ (with M–N = 2.00 Å)

	Configuration			
	D($\delta\delta\delta$)	D($\delta\delta\lambda$)	D($\delta\lambda\lambda$)	D($\lambda\lambda\lambda$)
(a) With Bartell's Equation				
$z_1 = z_2$	6.8	6.8	7.1	7.6
$z_1 = 0.2$ Å	6.8	6.1	7.3	8.2
$z_1 = 0.0$ Å	8.1	7.5	10.9	14.1
Relative energies	0.0	−0.7	0.4	0.8
(b) With Empirical Equation				
$z_1 = z_2$	3.6	3.7	4.0	4.5
$z_1 = 0.2$ Å	3.7	3.4	4.0	5.9
$z_1 = 0.0$ Å	4.8	4.6	8.1	11.6
Relative energies	0.0	−0.1	0.35	0.85

[a] In kcal mol^{-1}.

In addition, an attempt was made to fit an empirical set of van der Waals curves to the following conditions derived from the experimental conformational analysis: (i) the D($\delta\delta\delta$) and D($\delta\delta\lambda$) configurations have similar energy and (ii) these configurations are of the order of 1 kcal mol^{-1} lower in energy than the D($\lambda\lambda\lambda$). This was carried out by assuming curves of the same shape as Hill's interaction curves and displacing them incrementally along the radial axis. A further condition was applied that the accepted van der Waals interatomic distances had to lie between the (attractive) minimum of the nonbonded curves and the distance at which the interactions became significantly repulsive. The calculations were found to be quite sensitive to the curves used. The equations that gave a good fit to the above conditions are given by

$$E = -2.25\epsilon(r^*/d)^6 + 8.28 \times 10^5\epsilon \exp(-d/0.0736r^*)$$

where ϵ and r^* are the usual Hill parameters, $d = r - (r_{\min} - r^*)$, and $r_{\min}$ is the distance at which the energy is a minimum. For H···H interactions, $r_{\min} = 2.55$ Å; for C···H, $r_{\min} = 3.2$ Å. The minimum energies for the various configurations are presented in Table I.

For the *trans*-bis-ethylenediamine system, the two rings were allowed to adopt independently the complete range of symmetric and nonsymmetric conformations that have previously been found to correspond to the lowest energy for an unsubstituted ethylenediamine chelate ring.[9] For all these configurations, there were no significant nonbonded interactions between the atoms of the two chelate rings according to Bartell's or the empirically derived equations.

Discussion

It is clear from the results that neither Hill's nor Mason and Kreevoy's equations can account for the experimentally determined energy differences in the tris complexes. Hill's equations are unsatisfactory since they underestimate the strength of the interactions which are thought to determine these energy differences. Mason and Kreevoy's equations fail because they apparently overestimate these interactions leading to a preference for the D(λλλ) configuration. Corey and Bailar found, using the Mason and Kreevoy interaction equation, that the D(δδδ) configuration was lower in energy than the D(λλλ) by 1.8 kcal mol^{-1}.[1] The reversal is due to the fact that Corey and Bailar did not allow for ring distortions to reduce the very high nonbonded interactions. Indeed, it has been found here that the chelate rings need to flatten (to, say, $z_1 = -z_2 = 0.25$ Å with $\omega = 38°$) to minimize the total energy. This type of flattening has not been observed in the structures determined by X-ray analysis.

When Bartell's equations were applied to the mixed complexes, the relative energies calculated for the D(δδδ), D(δδλ), D(δλλ), and D(λλλ) configurations were found to be 0, −0.7, 0.35, and 0.8 kcal mol^{-1}. The predicted preference or the D(δδλ) over D(δδδ) derives mainly from the relief of H···H interactions in the nonsymmetric conformations ($z_1 = 0.2$ Å) of the D(δδλ) complex. The empirical equations were fitted to the experimental data by reducing the contribution of the H···H interactions to the total energy. The relative energies obtained using the empirical equations are 0, −0.1, 0.35, and 0.85 kcal mol^{-1}.

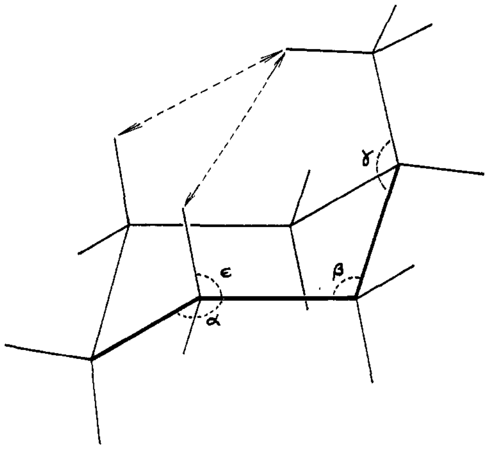

Figure 6.—Axial conformation of methylcyclohexane.

In order to test the validity of the empirical equations, they were applied to the methylcyclohexane system in an attempt to calculate the energy difference between the two conformations in which the methyl group is axial and equatorial. This energy difference has been well established experimentally as about 1.7 kcal mol^{-1}.[19] Early attempts to account for this energy difference were often misleading since they did not permit the structure to distort in order to alleviate large interactions. Here the structure was permitted to flatten in the manner shown (Figure 6) in order to relieve the interactions between the axial methyl group and the axial hydrogens. The minimum energy axial conformation had the following angles: $\alpha = 109.5°$, $\beta = 112°$, $\gamma = 112°$, and $\epsilon = 112°$. Using the above empirical equations, the calculated energy difference is 1.0 kcal mol^{-1}. The agreement between the calculated and experimental values, while imperfect, is reasonable in view of the basic differences between the complex system from which these equations were derived and the methylcyclohexane, and rather than perform a more elaborate curve-fitting procedure on the limited amount of data available, the empirical equations have been adopted for the purposes of the following discussion.

The four types of configurations for M(en)$_3$ differ in the range of conformations which may occur without significant change in energy. In the D(δδδ) {=L(λλλ)} configurations a large variety of conformational geometries correspond to the lowest energy. The range includes both symmetric and nonsymmetric conformations (including those with $z_1 = 0.35$ Å and $z_1 = 0.2$ Å). The range of nonsymmetric conformations is limited by significant interactions in the $z_1 = 0$ conformation. The proposed flexibility of the chelate rings in this configuration is consistent with the postulate of Saito,[4] who suggested from a consideration of the anisotropic thermal parameters of the ring atoms in *d*-[Co(en)$_3$]-Cl$_3$·H$_2$O that the two carbon atoms oscillate perpendicular to the C–C bond with a mean amplitude of 0.3 Å. The calculations have shown that the same flexibility is lacking in the D(λλλ) {=L(δδδ)} configuration. It is interesting to note that in D(δδλ) there is a slight preference for the type of conformation with $z_1 = 0.2$ Å and $z_2 = -0.4$ Å, which is the conformation that has been found in D(δδλ)-[Cr(en)$_3$][Ni(CN)$_5$].[5]

(19) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," John Wiley and Sons, New York, N. Y., 1965, p 439.

For M((*S*)-pn)$_3$, when the methyl groups are equatorial, the significant interaction system is identical with that for M(en)$_3$, and, therefore, the energy difference between the D($\delta\delta\delta$) and L($\delta\delta\delta$) configurations using the empirical equation is about 0.9 kcal mol^{-1}. For a complex of the type M((*S*)-pn)(NH$_3$)$_4$, interactions between the methyl group in an axial orientation and the ammonia groups can be somewhat relieved by the rotation of the NH$_3$ about the M–N bond.[9] This alleviation of the van der Waals interaction of the axial methyl group is not possible to the same extent in M((*S*)-pn)$_3$. Thus, the preference for the equatorial conformation (δ) will be greater for the tris than for the mono complex.

According to the present geometrical model, the relative energies of the three configuration types of the *cis*-bis-ethylenediamine complexes are (kcal mol^{-1}): D($\delta\delta$) = L($\lambda\lambda$), 0; D($\delta\lambda$) = L($\lambda\delta$), −0.05; D($\lambda\lambda$) = L($\delta\delta$), 0.3. However, it must be emphasized that this model probably overestimates the interactions because, for these complexes, nonbonded interactions with a third puckered conformation are missing, and the two chelate rings should be able to distort more than for the tris complex to alleviate any interactions between them. In fact, it is conceivable that the order of preference is in error because of this facility for distortion. Nevertheless it can be concluded from this study that the actual energy differences between the configurations is very small.

As stated in the Results the chiral and *meso* configurations of the *trans*-bis-ethylenediamine complexes have equivalent energies when Bartell's or the empirical equations are used. Corey and Bailar calculated an energy difference of about 1 kcal mol^{-1} using the Mason and Kreevoy H···H interaction expression without allowing for distortions of the chelate rings, which could considerably reduce even this energy. Therefore, conformational analysis suggests that the chelate rings are free to adopt either the chiral or *meso* configurations.

Finally, as the medium-energy interaction equations have been found to be the more realistic, it is possible to comment further on the energy differences between the axial and equatorial orientations of a methyl group in mono(N- and C-substituted ethylenediamine) complexes. The energies would approximate to those published using the Bartell equation.[9] For tetraammine((*R*)-propylenediamine)cobalt(III) the energy difference would be of the order of 0.7 kcal mol^{-1}, and, for the equivalent N-methylethylenediamine complex about 0.8 kcal mol^{-1} in favor of the equatorial orientation.

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Complexes of Tri-*n*-butylphosphine Oxide with Metal Perchlorates

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Complexes of tri-*n*-butylphosphine oxide (TBPO) with metal perchlorates were synthesized and characterized by means of spectral, magnetic, conductance, and X-ray powder diffraction studies. Coordination of monodentate perchlorate groups has been established for the Cr(III), Fe(II), Fe(III), and Ce(III) compounds, which are of the novel types [M(TBPO)$_4$(OClO$_3$)$_2$](ClO$_4$) (M = Cr(III), Fe(III), Ce(III)) and [Fe(TBPO)$_4$(OClO$_3$)$_2$]. Mg(II), Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) yield cationic complexes of the type M(TBPO)$_4^{2+}$. The Co(II) and Zn(II) complexes are tetrahedral. The Cu(II) complex may be assigned either a symmetry intermediate between distorted T$_d$ and D_{4h} or a polymeric hexacoordinated tetragonal structure, involving both terminal and bridging ligand molecules. Of interest are the Ni(II) and Mn(II) complexes, which, unlike their analogs with other phosphine oxides, have a distorted tetrahedral ligand field symmetry with essentially T$_d$ MO$_4$ moieties. The steric and inductive effects influencing the stereochemistry of metal complexes of neutral organophosphoryl compounds are discussed.

Introduction

Although metal complexes with phosphine oxides (R$_3$PO) are among the first complexes of monodentate oxo ligands to be synthesized,[1] systematic characterization studies of compounds of this type have appeared only in recent years. Several of these recent studies dealt with phosphine oxide complexes of metal perchlorates.[2-5] Cationic complexes of the general type ML$_4^{n+}$ (M = Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II)) have been reported for triphenyl-, trimethyl-, and triethylphosphine oxides (TPPO, TMPO, and TEPO, respectively).[2-4] Co(II) and Zn(II) complexes

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