Cluster and Molecular Mechanical Analysis of the Conformations of All Six-Membered Cobalt(III) Diamine Rings in the Cambridge Structure Database

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Received September 25, 1995⊗

An agglomerative, single-link clustering method was used to separate all of the cobalt(III) diamine six-membered rings found in the Cambridge Structural Database into chair, boat, unsymmetric twist-boat, and δ and λ twist-boat conformations. Of all of the six-membered rings analyzed, 80% adopt the energetically favored chair conformation. Twist boats are favored for steric reasons, while the high-energy boats are only found when the six-membered ring is structurally prevented from adopting a chair or twist-boat conformation. This is the first inorganic cluster analysis to published. The conformations of all of the nonchairs, except one, could be found by generating all of the possible combinations of the different idealized conformations of five- and six-membered rings and minimizing them.

Introduction

An agglomerative, single-link clustering method[1] was used to analyze the conformations of all the cobalt(III) diamine six-membered rings found in the Cambridge Structural Database (CSD).[2] To date, cluster analysis has been used in the study of large biomolecules[3] and molecular dynamics,[4] but it has not been used to investigate inorganic complexes.

Besides the obvious importance of a systematic analysis of the conformations adopted by six-membered cobalt(III) rings, we have undertaken this study to establish whether cluster analysis can be used to find significant groupings in small inorganic molecules.

The conformations of *organic* six-membered rings have been under investigation for more than a century.[5] A number of different methods have been devised to describe the conformations available to six-membered rings,[6] and several different clustering algorithms, applied in torsional space, have been used in the conformational analysis of six-membered carbocycles.[7] The potential energy differences between various conformations of six-membered carbocycles have been calculated,[8] and high-energy conformations have been synthesized.[9]

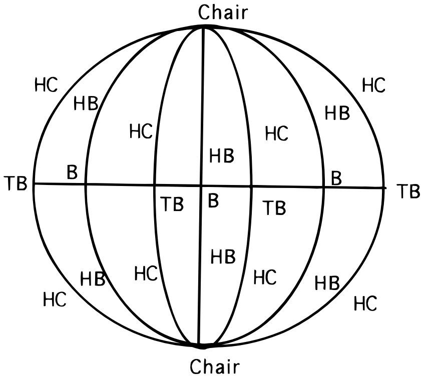

Figure 1. Spherical energy map for cyclohexane (HC = half-chair; HB = half-boat; B = boat; TB = twist boat).

The conformations adopted by cyclohexane are well-described by the spherical energy map proposed by Hendrickson and displayed in Figure 1.[6a]

The two poles of the sphere correspond to the chair conformations, while the twist-boat (tb) and boat conformations lie along the equator. Pseudorotational conformational changes are depicted horizontally (latitudinally) and symmetrical changes vertically (longitudinally). The energy barriers between the twist boat and the higher energy boat conformations along the pseudorotational path are very low, while the longitudinal barriers between the chair and boat or twist boat conformations are higher than the latitudinal ones and of comparable height to each other.[10] The two chair positions at the poles and the six equatorial twist-boats are energy minima, while the boat conformations are minima between the two chair forms (longitudinally) but saddle points between the twist-boat conformations (latitudinally).

The energy and symmetry properties of cyclohexane described above are not necessarily valid for inorganic six-membered rings as there are many different twist-boat and boat conformations with different energies and therefore the energy surface, shown in Figure 1, is no longer spherical.

A number of investigations into the possible conformations of 1,3-propanediamine (tn) complexes have been published. The most common conformations adopted by saturated six-membered chelate rings are shown in Figure 2.[11]

⊗ Abstract published in *Advance ACS Abstracts,* May 1, 1996.

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(4) (a) Karpen, M. E.; Tobias, D. J.; Brooks, C. L., III. *Biochemistry* **1993**, *32*, 412. (b) Gordon, H. I.; Somoraj, R. L. *Proteins: Struct., Funct., Genet.*, **1992**, *14*, 249.
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(6) (a) Hendrickson, J. B. *J. Am. Chem. Soc.* **1967**, *89*, 7047. (b) Cremer, D.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 1354. (c) Haasnoot, C. A. G. *J. Am. Chem. Soc.* **1992**, *114*, 882.
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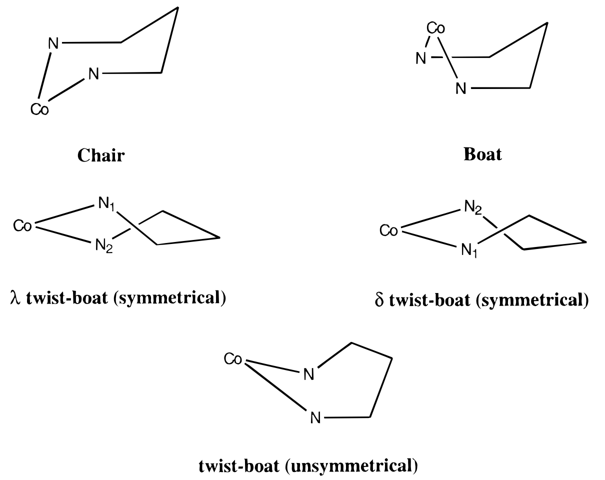
(8) (a) Allinger, N. L.; Hirsh, J. A.; Miller, M. A.; Tyminski, I. J. *J. Am. Chem. Soc.* **1969**, *91*, 337. (b) Dasgupta, S.; Tang, Y.; Moldowan, J. M.; Carlson, R. M. K.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1995**, *117*, 6532.
(9) (a) Columbus, I.; Cohen, S.; Biali, S. E. *J. Am. Chem. Soc.* **1994**, *116*, 10306. (b) Sieburth, S. M. *J. Chem. Soc., Chem. Commun.* **1994**, 1663.
(10) Strauss, H. L. *J. Chem. Educ.* **1971**, *48*, 221.

S0020-1669(95)01223-7 CCC: $12.00



Chair **Boat**

λ **twist-boat (symmetrical)** δ **twist-boat (symmetrical)**

twist-boat (unsymmetrical)

Figure 2. Common conformations adopted by six-membered chelate rings.

Some of the earliest inorganic molecular mechanics publications analyzed the conformations available to (propanediamine)cobalt(III) complexes. Studies of cobalt coordinated to a single propanediamine ring showed that the chair conformation is preferred over the twist-boat forms by about 12 kJ/mol and that the majority of the strain in the twist boats is caused by torsional deformations.[12] In complexes of the type $[Co(tn)_3(X)_4]$, where X is a small ligand, the 1,3-diaminopropane should therefore adopt a chair conformation. The energy barrier for a chair to chair interconversion was also shown to proceed through a twist boat form with a energy barrier of 24 kJ/mol.[12a]

The relative energies of the various conformations adopted by $[Co(tn)_3]^{3+}$ complexes are much closer, and there is some disagreement about the lowest energy form. Gollogly and Hawkins[12a] calculated that a tris chair form would be the lowest energy conformation, while Geue and Snow[13] predicted a tris twist-boat conformation. However, both of their calculations were incomplete as they did not consider the possibility of a complex containing both twist-boat and chair conformations in different rings. Subsequently, Niketic and Woldbye[12b] concluded that such a “mixed” complex is located at the global minimum.

Molecular mechanical analysis of (2,4-pentanediamine)cobalt complexes has shown that the twist-boat form in which both methyl groups are in the equatorial position is favored[14] over the chair conformer by 8.3 kJ/mol.[15] Even though the chair conformer is favored over the twist-boat forms on the basis of dihedral interactions, its highly strained valence angles and high-energy nonbonded interactions result in a higher strain energy than that calculated for twist boats.

Rasmussen and co-workers have crystallized and molecular mechanically analyzed a number of cobalt(III) propanediamine complexes with ethylenediamine and butanediamine coligands.[16] They have found that the twist-boat propanediamine ring has a 6−10 kJ/mol larger intrachelate strain energy than the chair form, which accounts for the observed preference of chair conformations in less-crowded complexes.

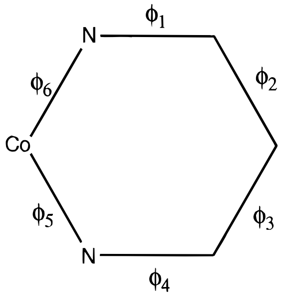


Figure 3. Six-membered cobalt(III) diamine fragment with dihedral angle labeling used in Table 1.

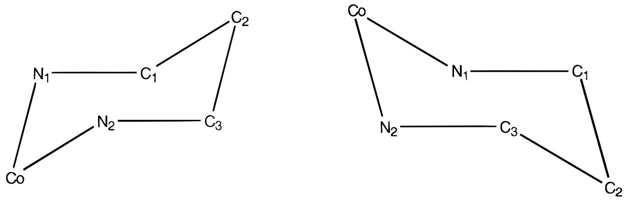


Figure 4. Example of two chair conformations that would be placed in separate clusters without symmetry adaption. However by reflecting N_1 and C_1 and N_2 and C_3 through the Co−C_2 axis, they can be compared.

Experimental Section

All structures containing cobalt(III) bound to propanediamine and propanediamine derivatives where both nitrogens and all of the ring carbons are sp^3 hybridized (see Figure 3) were found and saved using the quest function of the CSD.

CSD version 5.07 was searched, it contains 120 481 structures and was last updated in April 1994. All crystal structures containing error free atomic coordinate data and with R factors less than 10.00 were kept. A set of 180 hits were obtained, these are given in the supporting information. They were converted into the MacroModel format by the csdconv utility.[17] All of the atoms not belonging to the cobalt(III) diamine six-membered rings were deleted, and each six-membered ring was read into a large masterfile. Atoms were renumbered so that all six-membered rings were numbered consistently, and 208 rings were placed in the masterfile.[18] They were analyzed by the XCluster[1] program contained in MacroModel v4.5.[19] Proximity matrixes were generated by determining the pairwise distance between conformations using (i) the root mean squared (rms) displacement between pairs of identically numbered atoms after optimal rigid-body superimposition[20] and (ii) the rms differences between corresponding torsional angles. In order to prevent a misalignment of torsional sequences or atomic positions, all of the atom labels in the rings were reflected through the plane created by the cobalt ion and the carbon atom directly opposite it. A six-fold rotation such as the one required for six-membered carbocycles[21] is not needed due to the C_{2v} symmetry created by the cobalt diamine moiety of the six-membered rings. Without taking into account the symmetry inherent in the cobalt six-membered rings, symmetry related conformations would be placed in different clusters, see Figure 4.

Molecular mechanics minimizations were undertaken using MM2*[22] with previously published parameters for the cobalt ion.[23] Constraints

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(11) Hambley, T. W.; Searle, G. H.; Snow, M. R. *Aust. J. Chem.* **1982**, *35*, 1285.

(12) (a) Gollogly, J. R.; Hawkins, J. *Inorg. Chem.* **1972**, *11*, 156. (b) Niketic, S. R.; Woldbye, F. *Acta Chem. Scand.* **1973**, *27*, 621.

(13) Geue, R. J.; Snow, M. R. *J. Chem. Soc. A* **1971**, 2981.

(14) Niketic, S. R.; Woldbye, F. *Acta Chem. Scand.* **1973**, *27*, 3811.

(15) Hambley, T. W.; Hawkins, C. J.; Palmer, J. A.; Snow, M. R. *Aust. J. Chem.* **1981**, *34*, 45.

(16) (a) Niketic, S. R.; Rasmussen, K.; Woldbye, F.; Lifson, S. *Acta Chem. Scand.* **1976**, *A30*, 485. (b) Niketic, S. R.; Rasmussen, K. *Acta Chem. Scand.* **1981**, *A35*, 623. (c) Ohba, S.; Rasmussen, K. *Acta Chem. Scand.* **1994**, *48*, 189.

(17) csdconv, a program supplied with MacroModel and written by P. Bartlett, University of California at Berkeley.

(18) Many structures contained more than one symmetry unrelated six-membered ring; therefore there are more six-membered rings than cobalt(III) structures.

(19) Mohamadi, F.; Richards, N. G. J.; Guida, W. C.; Liskamp, C.; Caufield, C.; Chang, G.; Hendrickson, T.; Still, W. C. *J. Comput. Chem.* **1990**, *11*, 440.

(20) (a) Kabsch, W. *Acta Crystallogr.* **1976**, *A32*, 922. (b) Kabsch, W. *Acta Crystallogr.* **1978**, *A34*, 827.

(21) Allen, F. A.; Doyle, M. J.; Taylor, R. *Acta Crystallogr.* **1991**, *B47*, 29.

of 1000 kJ/mol were used for the V1 barrier in the torsional term, in order to determine the relative strain energies of the average conformation of each cluster. Conformational searches were undertaken, as described previously.[24] In order to obtain all of the possible combinations of the chair, boat, and twist-boat conformers for six-membered rings, and the λ and δ conformers for five-membered rings, starting geometries were generated with the draw function of MacroModel, and the endocyclic dihedral angles were constrained. The complexes were minimized, the constraints were released, and the structures were reminimized. Structures obtained in this manner were superimposed[20] with the solid state structure, to see if they adopted the same conformation as found in the crystal structures.

Results and Discussion

Clustering algorithms attempt to find groupings such that the similarities within the groups are significantly greater than those between groups. There are many different methods of clustering data. We used XClusters,[1] an agglomerative, hierarchical single-link clustering method, which means that we started with separate conformations and united them into clusters (agglomerative). If a pair of conformations were next closest in conformational space, they were joined in a cluster (single link), and if the pair of closest conformations were in adjacent clusters, they were fused (hierarchical). Although this is an effective method of clustering conformations it has one drawback[25]—separate clusters can become linked by isolated structures that bridge the outlying members of two clusters. In this study we are clustering conformations of six-membered rings derived from crystal structures, we can therefore assume that these conformations are low-energy conformations. If the low-energy conformations are separated by a large energy barrier, for example, the barrier between the boat and the chair conformations, bridging of clusters by outlying conformations in single-linkage clustering is not a problem. However, if the energy barrier is small, such as that found between the boat and twist-boat conformations, separate clusters can be joined by outlying conformations that span the energy barrier, and single-linkage clustering might not be appropriate. We will show that this was not a problem in the clustering of the six-membered cobalt(III) diamine rings and that single-linkage clustering can distinguish between the idealized six-membered conformations given Figure 2.

Figure 5 shows the mosaic diagram obtained by performing a cluster analysis of the endocylic torsional angles of all 208 cobalt(III) six-membered rings. Mosaic diagrams are similar to the more commonly seen clustering dendritograms. The top level of the mosaic shows all the rings in 208 separate clusters, in the second highest level the two rings with the closest torsional distance between them have been joined to make the first cluster. This process is repeated, and in each clustering level two more conformations are joined, if the two rings are in different clusters, the two clusters are joined to form one large cluster, until at the bottom of the mosaic, in clustering level 208, all of the conformations have been joined into one large cluster. At each clustering level a horizontal line is placed over conformations that have just been joined.

The clustering mosaic, Figure 5, shows that at high clustering levels the majority of rings belong to a single large cluster on the left of the figure and that the remainder belong to several smaller clusters. The same clustering behavior is observed in the distance map, Figure 6,[26] which is a visual representation of the torsional distance matrix where shorter distances are indicated by darker shades. The figure shows that there is a single large cluster which contains 166 of the rings. The torsional distances between the members of this cluster are very small, and they are all significantly different from the nonmembers. Such a significant difference between separate clusters is found at clustering levels 196−202. In Figures 5 and 6 we have labeled the individual clusters at clustering level 200.

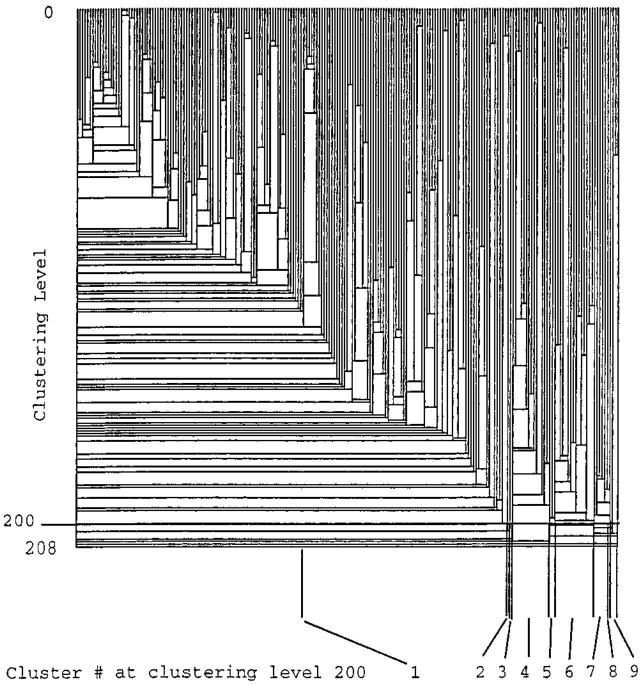

Figure 5. Clustering mosaic for cobalt(III) six-membered rings.

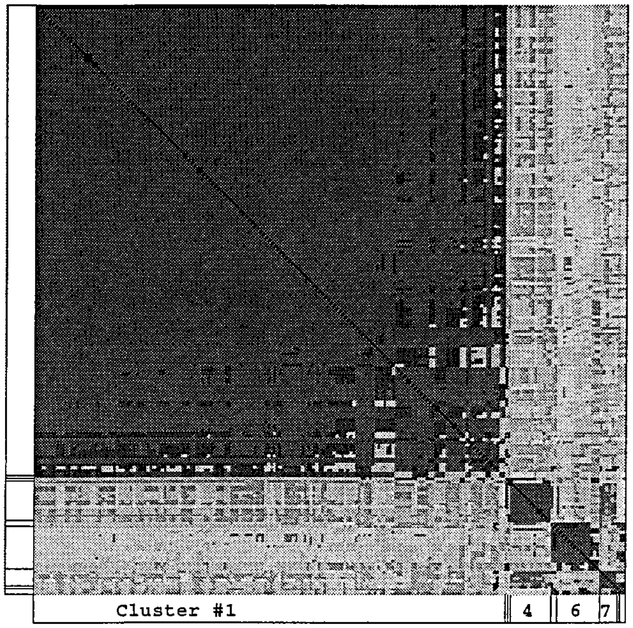

Figure 6. Torsional distance matrix described in text.

Structural similarity is not always correlated to the difference in dihedral angles, as a small change in a single dihedral angle can, due to leverage effects, lead to large structural changes. Furthermore, two large differences in dihedral angle can cancel

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(22) Allinger, N. L.; Yuh, Y. H.; Lii, J.-H. *J. Am. Chem. Soc.* **1989**, *111*, 8551 (as implemented in MacroModel 4.1).

(23) Charles, R.; Ganly-Cunningham, M.; Warren, R.; Zimmer, M. *J. Mol. Struct.*, **1992**, *265*, 385.

(24) Spence, K. L.; Tueting, J. L.; Zimmer, M. *J. Chem. Soc., Dalton Trans.* **1994**, 554.

(25) Torda, A. E.; Van Gunsteren, W. F. *J. Comput. Chem.* **1994**, *12*, 1331.

(26) Color representations of Figures 6 and 7 and conformational superimpositions of the major clusters can be found at http://camel.conncoll.edu/ccacad/zimmer/MZ-8/MZ-8.

Table 1. Average Torsional Angles, Strain Energy, and the Number of Members for Each Cluster, at Clustering Level 200[a]

cluster	ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_5	ϕ_6	energy (kJ/mol)	no. of members	conformation
1	−66.9	67.7	−61.7	57.9	−48.4	50.4	12.86	166	chair
2	6.3	47.2	−81.7	48.7	−0.4	−27.5	37.20	1	λ unsymm tb
3	46.3	−68.1	21.0	38.0	−46.9	4.8	29.07	1	λ tb
4	64.9	−35.2	−30.0	64.9	−33.4	−29.4	24.63	14	λ tb
5	−13.9	−53.0	76.8	−23.5	−30.0	50.9	40.07	2	boat
6	−13.9	−63.0	70.5	0.80	−56.5	64.0	59.46	15	boat
7	−57.0	17.7	46.0	−63.4	23.0	34.3	27.86	6	δ tb
8	−44.8	76.1	−25.1	−43.2	59.0	−12.2	28.45	1	δ unsymm tb
9	−37.2	−36.9	82.8	−37.4	66.5	−30.3	176.01	2	δ unsymm tb
ideal chair	−60.0	60.0	−60.0	60.0	−60.0	60.0	16.28		chair
minichair[b]	−63.6	60.2	−60.2	63.6	−52.8	52.8	8.15		chair
ideal boat	0.0	−60.0	60.0	0.0	−60.0	60.0	170.53		boat
ideal tb	60	−30	−30	60	−30	−30	27.58		tb
miniboat[b]	69.3	−34.1	−34.1	69.3	−33.0	−33.0	20.69		tb

[a] The torsion angles are numbered as shown in Figure 3. [b] Co(tn) minimized from ideal boat/chair conformation. All others were minimized with torsional constraints.

each other, resulting in two unrelated structures being placed in the same cluster. However, since we are comparing symmetry adapted *rings*, these two problems should not be important. Indeed, there is no significant difference between the clustering pattern obtained when the rms difference between the atomic coordinates was used as a measure of conformational difference in place of the dihedral angles.

On the basis of the cluster mosaic, Figure 5, and the distance map, Figure 6, we have analyzed the conformations of six-membered rings at clustering levels 196−202. In this paper we will describe our findings at clustering level 200 as it is representative of all of the other significant clustering levels investigated. The average torsional angles, the number of members in all of the clusters, and the torsional angles of idealized boat and chair conformations are given in Table 1. The nonchair clusters can be divided into four different groups: the boats, the λ and δ twist boats, and the unsymmetrical twist boats. Even though cluster 1 is made up only of chairs and cluster 6 of boats, their average torsional angles deviate quite significantly from the ideal cyclohexane values; this is due to the octahedral geometry around the cobalt(III) ion and the cobalt−nitrogen distances, which are longer than the carbon−carbon distances in cyclohexane. We confirmed this by minimizing an isolated cobalt(III) propanediamine ring from an ideal chair conformation. The resulting conformation has similar internal torsional angles as the average dihedral angles of cluster 1 and is clearly still a chair, see Table 1. A conformational search revealed that this conformation is located at the global minimum. Only one other minimum was located in the search, a twist boat, which was also obtained when minimizing cobalt(III) propanediamine with an ideal boat conformation. The dihedral angles of this twist-boat conformation are similar to those of cluster 4 and are given in Table 1. As is the case for cyclohexane, the boat conformation is a minimum between the two chair forms and a saddle point between the two twist boats.

The Co−N−C angles of the boats are much closer to the expected tetrahedral angles than those of the chairs and twist boats. Although this is energetically favorable, it is counterbalanced by the eclipsing of two endocyclic dihedral angles. Further analysis of the average bond lengths and angles of the various clusters are unrevealing.

Of the six-membered rings, 80%, that is, 166 of 208 at clustering level 200, are in either chair or distorted chair conformations. They all belong to cluster 1. Not only was XCluster able to separate the chair conformations from all of the boat and twist-boat conformations, as Table 1 shows, it was also able to distinguish between different boat conformations. These are distributed as shown in Table 2. At none of the clustering levels between levels 196 and 202 do any of the four conformations join the same cluster. However, the individual conformations are split apart, for example, in clustering level 200 one of the λ twist boats (cluster 3) is separated from the other λ twist boats (cluster 4), there are two sets of boats (clusters 5 and 6), and the unsymmetrical twist boats are spread among three clusters.[26]

Table 2. Distribution of the Four Main Conformations

conformation	no. of members	no. of members due to sterics only	energy (kJ/mol)
chair	166	166	9.89
λ and δ twist boats	21	20	21.62
boat	17	0	59.75
unsymm twist boat	4	2	26.25

In order to establish some energetic relationship between all of the clusters we have minimized cobalt(III) propanediamine fragments with their dihedral angles constrained to the average torsional angles of each individual cluster. The energies obtained in this manner are given in Table 1. Using restraints[27] in place of constraints would have been more accurate, but since the energies of cobalt(III) propanediamine fragments were calculated without considering the individual ligand structures or the identity of the other ligands coordinated to the cobalt, we considered the small errors introduced by using constraints negligible in comparison to the those introduced by the other simplifications made. Despite the approximations described above, the energies for the average cluster conformations are useful descriptors. The strain energy for the average chair conformation in cluster 1 is 12 kJ/mol lower than that of the average λ twist boat in cluster 4. This energy difference compares remarkably well with the energy difference obtained between the minimized ideal chair and twist boat, and it also agrees well with previously determined values.[12] As expected the energies of the boat and unsymmetric twist boats are at least 15−30 kJ/mol higher than the average chair conformation.

Figure 7 shows the structures of all of the cobalt(III) complexes that were found in clusters 2−9. There are three possible reasons these compounds adopt high-energy nonchair conformations: sterics, structural constraints in which the ligand is not able to adopt a chair conformation; and intermolecular forces. The majority of nonchair conformations adopted for steric reasons are due to the preference for equatorial methyl

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(27) Comba, P.; Hambley, T. W. *Molecular Modeling of Inorganic Compounds*; VCH: Weinheim, Germany, 1995.

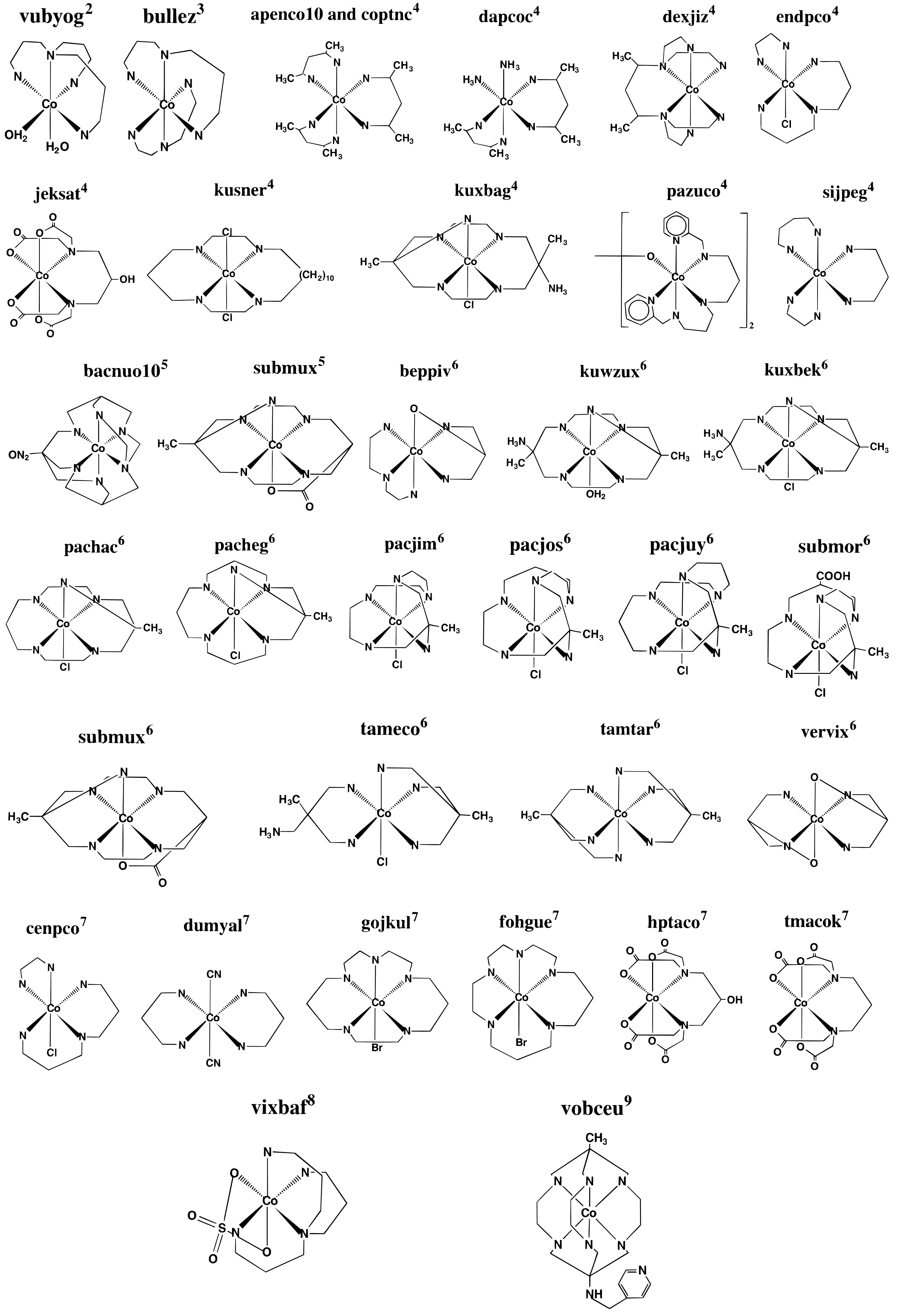
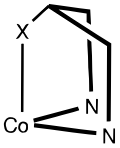


Figure 7. Structures in clusters 2−9 (cluster membership given as superscripts to CSD refcodes).

groups in 2,4-pentanediamine ligands and its derivatives (apenco10, coptnc, dapcoc, and dexjiz) and due to interligand repulsions (vubyog, bullez, endpco, sijpeg, cenpco, and vixbaf). On the other hand all of the members of clusters 5 and 6 are examples of rings that adopt high-energy boat conformations because the coordination of a pendant arm linked to the six-membered ring structurally prevents the adoption of a chair conformation, see the following structure.



The strain energies of cobalt(III) propanediamine rings with structurally imposed nonchair conformations are higher than all those formed due to steric interactions. Table 2 lists how often each of the different conformations, shown in Figure 2, occurs and how many of these occurrences are due to steric reasons. Not surprisingly a correlation between strain energy and occurrence exists. This should not be overinterpreted as the calculated energies are those of the average conformation of the major cluster containing the conformation in question.

One of the aims of this analysis was to establish whether inorganic molecular mechanical calculations of molecules involving six-membered rings could be done by minimizing all of the possible combinations of chair, twist boats, and boats or whether a conformational search had to be undertaken in which the internal dihedral angles of the six-membered rings were varied. In the vast majority of inorganic molecular mechanical analyses no conformational searches are undertaken. In fact in a recent review of bioinorganic molecular mechanics it was found that less than 10 of the 126 studies being reviewed undertook a conformational search.[28] Instead, it is common practice to enter all probable structures individually and minimize them separately or to minimize the crystal structure and ignore all other possible conformations. The possible structures are generated by drawing all possible combinations of the chair, boat, and twist-boat conformers for six-membered rings and λ and δ conformers for five-membered rings. Isomers and stereoisomers are handled in the same way.[29] In order to establish whether this approach was a valid one, we have minimized the conformations of at least one complex from each cluster and compared the minimized structures with the crystal structure. In clusters containing more than one complex, we chose to minimize cobalt(III) compounds that could be minimized with our existing force field parameters.[24] Starting geometries were drawn and the six-membered rings were constrained to the idealized chair, boat, or twist boat nearest to the conformation observed in the solid state. The structures were minimized before releasing the constraints and reminimizing. In all of the cases we investigated, only two of the structures obtained in this way did not corresponded to that of the crystal structure. In cenpco and dumyal the solid state structure could only be found by undertaking a conformational search, as there were local minima located between the starting geometry and the structures obtained by drawing all of the possible combinations of the idealized conformations. In all cases, excepting dumyal, in which there were two lower energy minima (a chair/chair and a chair/twist-chair), the solid state structure and the lowest energy structure were identical. The lowest energy structure of kusner was found by constraining the five- and six-membered rings in ideal conformations and using a Monte Carlo dihedral angle search to find the conformation of the fifteen-membered ring.

Conclusions

This is the first cluster analysis of inorganic compounds. The technique is very effective; not only was cluster analysis able to differentiate between the different conformations adopted by cobalt(III) propanediamine rings, it was also able to distinguish between conformations that were formed for steric reasons and those that are unable to form chairs for structural reasons. The method is very useful in analyzing small inorganic compounds and could be used in many important problems, such as investigating the nonplanar deviations of porphinoid compounds.[30] We found that 80% of all cobalt(III) six-membered-ring complexes adopt a chair or distorted-chair conformation and that boat conformations are only found when the six-membered rings are structurally constrained by ligation of a pendant arm. We have also shown that in the vast majority of cases minimization of the structures generated by using all possible combinations of idealized conformations will lead to the global minimum.

Acknowledgment. We would like to thank the Keck Foundation for a summer fellowship for M.F.D. and Bridget Baird for programming help.

Supporting Information Available: One table containing references, CSD names, and cluster membership of all six-membered rings analyzed (8 pages). Ordering information given on any current masthead page.

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