Conformational Analysis of Coordination Compounds.

VII. Potential Energy Surface and Mechanism of Ring Inversion in Tris(1,2-ethanediamine) Complexes

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The ring inversion in $M(en)_3$ is studied by energy minimization methods. The potential energy surface for inversion is charted and the path on the surface is found. The three rings move independently of each other. The saddle point of a chelate ring is a symmetrical envelope with carbon atoms 0.7 Å from the NMN plane. The barrier height is 30 kJ mol^{-1} for the $ob \rightarrow lel$ process and 35 kJ mol^{-1} for the reverse. The inversion can be described by one two-dimensional vibration at 127 cm^{-1}; the two normal coordinates are shown in stereo. The rates of inversion are estimated at 21 MHz for the $ob \rightarrow lel$ process and 3 MHz for the $lel \rightarrow ob$.

The equilibrium conformations of $[Co(en)_3]^{3+}$ were investigated in papers IV [1] and VI [2] of this series. In the former, energy minimization in a fairly simple force field was used to obtain structural details, and in the latter differences in thermodynamic functions were calculated, leading to conformer distributions at equilibrium in agreement with data derived from experiment.

Whereas that work was mainly of a reproductive (or postdictive) nature, we report here a study which is essentially predictive, an investigation of the path in conformational space taken by a chelate ring when changing from *lel* to *ob* conformation or *vice versa*. From these results we derive the barrier towards ring inversion and the shape of the potential energy surface for inversion. This leads to a conclusion on the normal modes involved and to an estimate of inversion kinetics.

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METHODS AND RESULTS

Nomenclature. In the following, *lel* and *ob* are used to label the equilibrium enantiomeric conformations of 5-membered en chelate rings in $M(en)_3$. Other conformations of en rings are defined using standard symmetry labels. Thus C_s is a regular envelope folded along N---N to the extent that the distance of both C-atoms from the N−M−N plane is $|z| > 0$ Å. The limiting case of the envelope with $z = 0$ Å is a C_{2v} (planar) conformation.

Choice of initial conformations. From symmetry considerations (with the help of molecular models) it is clear that the transition state in the $lel \rightleftarrows ob$ inversion must correspond to an eclipsed situation around the C−C bond and, therefore, to an envelope conformation. In an attempt to pinpoint the saddle point which should correspond to the transition state for the $lel \rightleftarrows ob$ interconversion, we have constructed a series of $M(en)_3$ structures in which one of the en rings is fixed in an envelope; the conformations range from $z = 0.0$ to $z = 1.0$ Å. This is done semi-manually, starting from, for example, the C_{2v} conformation of the ring, folding it stepwise by varying the dihedral angle between the NMN and NCCN planes from 0° ($z = 0.0$) to approximately 46° ($z = 1.0$ Å), and recalculating cartesian coordinates for C and H atoms using standard matrix methods. The C_s conformations generated in this way are used as starting points in energy minimization procedures (described below).

Force Field. The force field employed in this study is the same as the one used in our previous work.[1] Although this force field can obviously be improved by readjustment of some of the potential energy parameters, we have adhered to it because we want (a) to retain the possibility of direct comparison of the present results with our former work, and (b) to further assess the applicability of this force field to a

new type of problem. The emphasis in this work is thus on the methodology of conformational interchange studies and not on the potential energy function.

Minimization. As is usual in our work, all minimizations are carried out with complete relaxation of all atomic coordinates. A full documentation of the complex of programmes used in the energy minimization is available elsewhere.[3] For the purpose of following in detail the progression of a minimization, a small modification is made: after each iteration all atomic cartesian coordinates are written on tape. A separate small programme has been written, which for each iteration reads the geometry from the tape and calculates the relevant internal coordinates such as torsional angles and distances of carbon atoms from the NMN plane of the same ring.

Steepest-descent minimizations. All initial minimizations are performed by the method of steepest descent. In this study we have taken full advantage of the steepest-descent algorithm, particularly its initial speed and its extremely slow convergence. The method proves to be very efficient in adjusting all bond lengths and valence angles to their optimal and normal values. Due to the choice of initial C_s conformations, most of which are high up on an energy scale, we are able, by the steepest-descent technique, to bring them very close to the saddle point regions on the potential energy hypersurface.

After "hitting" the surface the steepest-descent algorithm practically does not move the atoms at all as is clearly shown by the torsional angle around the $C-C$ bond in a C_s ring which initially is $0°$ and remains $<1°$ after steepest-descent minimization in all runs. In this way we end up with a series of $M(en)_3$ conformations with one en ring being practically C_s, with z ranging from 0.0 to 1.0 Å, all having the norm of the gradient about $2-5$ kJ mol^{-1} Å^{-1}. Whereas the torsional angles show that we are very close to saddle points in torsional angle subspace, the low gradient norms assure that this is indeed true in the entire conformational space. Just one misplaced hydrogen atom would give a much higher gradient norm. This is achieved with from 10 to 25 iterations.

As this series of conformations corresponds to a series of points on the potential enrgy surface along the ridge separating *lel* and *ob* minima, this procedure serves to locate approximately the conformation corresponding to the transition state for the, *lel*⇄*ob* interconversion process.

Modified Newton minimization. From each point reached by steepest-descent we perform minimization by the modified Newton method. This procedure brings all conformations quickly to their

equilibria, using typically between 12 and 20 iterations. This minimization algorithm differs from the former in its ability to follow closely and efficiently the valleys on the potential enrgy surface leading to minima. In this way we are able to perform a mapping of the surface and, by doing this from a wide range of points along the ridge, we obtain a sufficient number of points over a wide area on the potential surface, from which data we may reconstruct the essential features of the surface relevant to the description of the *lel*⇄*ob* interconversion process.

Graphical representation of the potential energy surface. Another feature of the minimization strategy described above is that the steepest-descent procedure changes practically only the stiffest internal variables, bonds and valence angles, while the modified Newton procedure changes essentially only the torsional angles in that ring which originally was forced into an envelope conformation. Therefore it is possible to represent the entire *lel*⇄*ob* interconversion in a torsional subspace of one ring only.

We choose the distances of the two carbon atoms of the flipping ring from a plane defined by the NMN atoms of the same ring as ring puckering coordinates, which we represent by two mutually perpendicular axes, z_1 and z_2. On such a graph C_s envelopes lie on the $z_1 = z_2$ line, C_{2v} in the origo, and equilibrium *lel* or *ob* conformations of C_2 symmetry at $\pm z_1 = \mp z_2 \approx 0.36$ Å. Each of $10-12$ Newton minimization performed from different starting points for, say, $M(en)_3$ (*lel*)$_2$(C_s) provides us with at least 10 useful points on the potential erergy surface. Where necessary, additional points are constructed by cubic spline interpolation of "experimental" points, assuming that the potential energy is locally smooth. A graphical representation of these results is made with the help of the GPGS package,[4] specifically its utilities GRAPHISTO[5] and SURRENDER,[6] which produce contour plots of the potential energy over the (z_1, z_2) subspace, and a perspective spatial representation of the potential energy surface, respectively.

Calculation of the rate of inversion. When the potential energy surface has been charted, inspection allows for identification of the vibration primarily involved in ring inversion. Comparison with plots of the normal coordinates[7] confirms the identification. From the barrier height and the frequency of the dominant vibration, we calculate the rate of inversion by unimolecular transition state theory. This collection of methods is a refinement of a procedure applied to the calculation of saddle points for conformational interchange in disaccharides.[8,9]
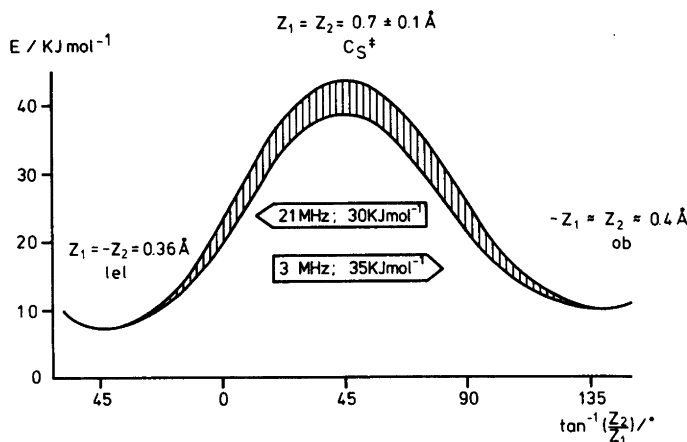
Fig. 1. Projections on the (z_1, z_2) plane of paths of ring inversion. Numbers on paths denote energies in kJ mol^{-1}.

DISCUSSION

The path on the potential energy surface. In Fig. 1 we present a selection of the minimizations. A ring conformation is represented by a point in the (z_1, z_2) subspace. The number associated with a point gives the energy of that ring conformation in kJ mol^{-1}. Any point in the (z_1, z_2) plane shows directly the ring conformation. Along the line $z_2 = -z_1$ we find the C_2 twist-chair conformations, along $z_2 = z_1$ the C_s envelope conformations, and at $z_1 = z_2 = 0$ the C_{2v} planar conformation. The numbering convention is such that, with Λ absolute configuration, rings with $z_1 > 0$ and $z_2 < 0$ have δ or *lel* conformation, and rings with $z_1 < 0$ and $z_2 > 0$ have λ or *ob* conformation. All initial conformations lie on $z_2 = z_1$. The final minima lie strictly on $z_2 = -z_1$ if the complex has the symmetry D_3, as for *lel*$_3$ and *ob*$_3$ conformations, and very close, if an exact C_3 axis is missing, as for *lel*$_2$*ob* and *lelob*$_2$.

It is clearly seen from the symmetry of the paths that a C_s or C_{2v} ring tends to one of its two C_2 minima independently of the conformations of the other two rings in the complex, *lel*$_2$, *lelob* or *ob*$_2$. This shows that, at least in the force field used here, the change in one ring is idenpendent of the conformations of the other rings, which implies that

the three rings move independently of each other. This conclusion corroborates observations from vibrational spectra of complexes with mixed coordination spheres.[10]

No matter which starting point on $z_2 = z_1$ is chosen, the conformational path towards minimum may be described qualitatively as a shift of one carbon atom away from the NMN plane. Thereupon the other carbon atom moves abruptly to the minimum energy position simultaneously with adjustment of the first. The minimum is in the region $(z_1, z_2) = (0.36|0.40, -0.30|0.36)$. Examining the energies of the intermediate conformations for each path, we find that the energetically most favourable path between *ob* and *lel* conformations must cross the $z_2 = z_1$ linear near $(0.7, 0.7)$, which is therefore the saddle point. The saddle point conformation is thus a pronounced envelope.

Fig. 2 shows a one-dimensional representation of the path of inversion. From the numbers given there we find a barrier for *lel* → *ob* inversion of 35 kJ mol^{-1} and for *ob* → *lel* inversion of 30 kJmol^{-1}. The uncertainties in the barriers, as expressed in the "smeared" curve of Fig. 2, are estimated from the results leading to Fig. 1: They are differences in

Fig. 2. Calculated pathway for $lel_3 \rightleftarrows lel_2ob$ interconversion in $M(en)_3$, with estimated uncertainty.

energy between points close in (z_1, z_2) space, but belonging to different series of minimizations.

Shape of the potential enrgy surface. From the many points calculated which, as argued above, fall on the potential energy surface, it is possible to obtain a graphical impression of its shape. This is done in Fig. 3, which shows a trough-like valley with an elongated bottom curving gradually away from the normal to $z_2 = -z_1$ at the bottom.
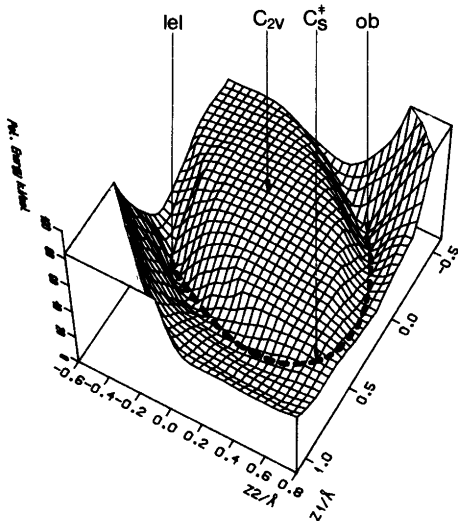
Fig. 3. Calculated potential energy surface for $lel \rightleftarrows ob$ chelate ring interconversion in $M(en)_3$. Estimated maximum uncertainty in energy is ± 2 kJ mol^{-1} near the saddle points.

Normal coordinates of inversion. Two distinct curvatures are seen at the bottom, largest along $z_2 = z_1$, much smaller along the shallow bottom. This implies that a low-frequency two-dimensional vibration is almost exclusively responsible for the movement leading to inversion, whereas a somewhat higher one-dimensional vibration does not contribute. Our charting of the surface is not sufficiently accurate for a calculation of its curvature, but a normal coordinate analysis has been performed, using the same force field,[7] and we find there an E vibration at 127 cm^{-1}. Fig 4 shows stereo plots of the classical amplitudes of its two normal coordinates. The movements towards the saddle point are clearly seen. It is also seen that the same vibration is described equally well by the movement of essentially one ring and of essentially two rings. This confirms the conclusion drawn from inspection of Fig. 1, that a ring inverts independently of the conformations of other rings.

The rate of inversion. From knowledge of the inversion barrier heights, 30 and 35 kJ mol^{-1}, and the one frequency involved, 127 cm^{-1}, we may estimate the inversion rate. The barriers are given as differences in totential energy, to which we ought to add differences in zero-point energy. We are presently not able to calculate the zero-point energy of a saddle point, but only of the four equilibrium conformers. They amount to 901.14, 901.11, 901.21 and 901.55 kJ mol^{-1} for $lel_3, lel_2ob, lelob_2$ and ob_3. In view of the other approximations made, we leave out the zero point corrections. Using the expression $k = v \exp(-\Delta E/RT)$, we obtain the rates $lel \rightarrow ob$ 3
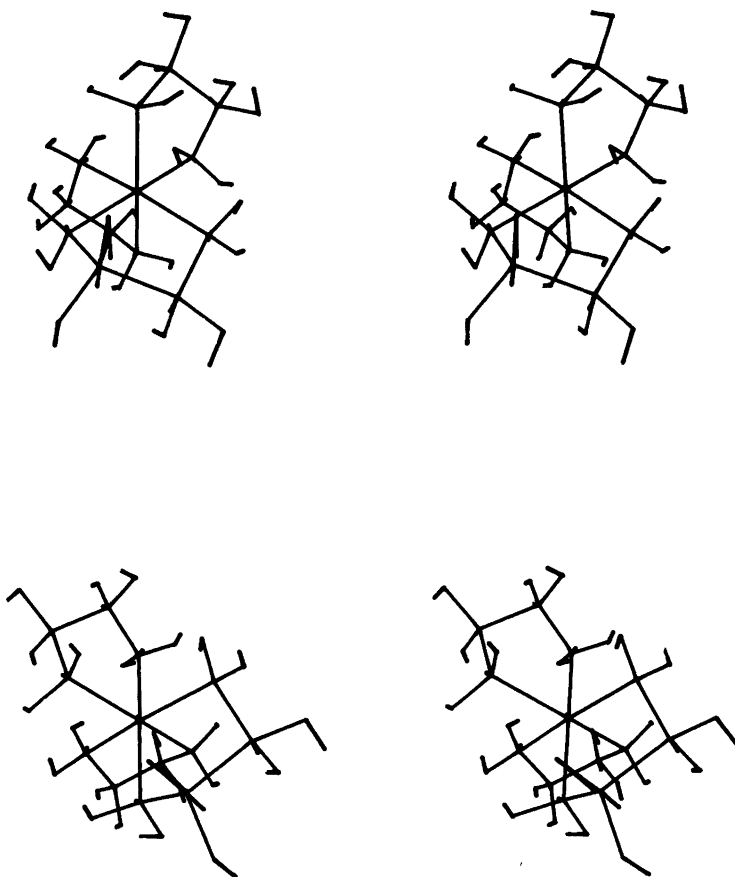
Fig. 4. Stereo view[13] of the two normal coordinates spanning the E ring-flip vibration in $M(en)_3$ *lel*$_3$.

MHz and *ob*→*lel* 21 MHz. These rates would seem to apply to inversion of five-membered en chelate rings in general, see the following section. The reader should not confuse the inversion of a ring conformation with the inversion of the absolute configuration of the complex as a whole, which involves either the breaking and making of coordinative bonds, or concerted or consecutive motion of all rings.

Comparison with experimental observations. One mostly finds statements like "the δ,λ-interconversion is rapid on the NMR time scale". Hawkins and coworkers[11] determined activation parameters for ring inversion in $[M(CO)_4(tmen)]$, where M was Cr, Mo, W and tmen N,N,N′,N′-tetramethyl-1,2-ethanediamine, by NMR measurements. They derived $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta G^{\ddagger}$;

$\Delta S^{\ddagger}$ with large uncertainty. Supposing the main characteristics of a chelate en ring being conserved from one complex to another, we may compare our ΔE with their $H^{\ddagger}$. Our values are $\Delta E^{\ddagger} = 30$ and 35 kJ mol^{-1}; the experimental data are $\Delta H^{\ddagger} = 39$, 42 and 38 kJ mol^{-1} for the three complexes. We deem the accord satisfactory. We are not able to calculate thermodynamic functions at the saddle point with our methods which require that a conformation be at an energy minimum. Therefore we cannot check against the measured $\Delta S^{\ddagger}$ which averages to 0 for the set of three complexes.

Comparison with previous calculations. At an early stage in the application of force field calculations to conformational problems in coordination chemistry Gollogly *et al* published a study on five-membered diamine chelate rings.[12] Using a rather crude model,

they reached qualitatively the same conclusions as in the present study.

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