distilled before being introduced into the autoclave from a weighed stainless steel vessel of ~250-ml capacity. The autoclave was then heated and the contents were stirred with a paddle speed of ~1000 rpm (see Table I for conditions and reaction times). After reaction was complete, the system was cooled to room temperature and the excess ammonia was allowed to evaporate through a toluene scrubber. A vacuum was applied through the scrubber to the autoclave and the organic product was distilled into the cooled solvent. The organic products were determined quantitatively by glpc (see Table I) and identified by infrared and mass spectrometric analyses. Hydrocarbon material balances were 97–99.5%.

Crude ytterbium amide remaining after distillation of ammonia and the organic products in expt 2 was a lavender-brown solid which when heated in a closed capillary tube became yellow at 400° and orange at 425° without melting. The ytterbium content of the amide was determined by neutral activation analysis.

Anal. Calcd for $Yb(NH_2)_2$: Yb, 84.4; N, 13.6; H, 2.0. Calcd for $Yb(NH_2)_3$: Yb, 78.3; N, 19.0; H, 2.7. Found: Yb, 82.8; N, 13.6; H, 2.3; C, 0.6.

Europium amide collected similarly from expt 1 was a gold-colored solid with mp >425°. The europium content of the amide was determined by neutron activation analysis.

Anal. Calcd for $Eu(NH_2)_2$: Eu, 82.6; N, 15.2; H, 2.2. Calcd for $Eu(NH_2)_3$: Eu, 76.0; N, 21.0; H, 3.0. Found: Eu, 82.6; N, 12.6; H, 2.3; C, 1.8.

The reduction of benzene under "Birch conditions" (expt 5) was performed at atmospheric pressure in a round-bottom flask equipped with a stirrer, gas-inlet tube, and Dry Ice condenser. The flask containing 0.13 g-atom of ytterbium turnings was cooled in a Dry Ice–acetone bath and ~250 ml of liquid ammonia was introduced by distillation. The dark solution was allowed to warm to the reflux temperature of ammonia (~−33°) and then 0.12 mole of benzene was injected. After 3.5 hr of stirring, the solution still remained dark indicating that little reaction had occurred. Ethanol (0.86 mole) was added and the mixture turned reddish brown. *n*-Pentane was added and the flask was allowed to warm to evaporate the ammonia. Water and then 10% hydrochloric acid were added to dissolve the solid. The hydrocarbon layer was separated, washed with water, dried over calcium chloride, and analyzed by glpc. The normalized product composition is listed in Table I. The material balance for the organic products was only 76.3%. This indicates that some material was lost during the evaporation of the ammonia and the extraction process.

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Correspondence

Intramolecular Isomerization of Octahedral Complexes by Mechanisms Not Involving Bond Rupture

Sir:

Two intramolecular isomerization mechanisms for octahedral complexes that do not involve bond rupture have been suggested.[1,2] These were originally proposed for chelate compounds and will be referred to hereafter as the Rây and Dutt and the Bailar twists, respectively.

The Rây and Dutt twist for a simple tris chelate complex is shown in Figure 1. If one of the rings is imagined to remain fixed in space, the motion can be described as the rotations of the remaining two rings 90° in opposite directions about axes perpendicular to their respective planes and passing through the metal ion. The rings remain rigid throughout the twisting process with the ring donor–metal–donor (D–M–D) bond angles remaining constant at approximately 90°. This motion is seen to result in optical inversion. The designations of absolute configuration used in this discussion are those of Piper[3] and Legg and Douglas.[4]

The Bailar twist for the same molecule as viewed along the C_3 axis is pictured in Figure 2. The motion of this mechanism may be described as the rotation of the three metal–donor bonds extending down from the plane of the paper (dotted lines) 120° about the C_3 axis in a counterclockwise direction. There results a contraction of the ring D–M–D bond angles (α) and consequent distortion of the chelate rings in the transition state. If this contraction is too great, the angle can expand back to a more favorable value only at the expense of the adjacent D–M–D angles (β) between donors in different rings. For the situation in which all D–M–D bond angles are equal in the trigonal prismatic transition state (*i.e.*, $\alpha = \beta$), values of 81° 48′ are required.[5] This motion also results in optical inversion.

An important difference, then, is seen to exist between the Rây and Dutt and the Bailar twists as originally proposed. In the former, the chelate ring internal angles do not change throughout the transformation, but do in the latter. In addition, in Bailar's mechanism, all of the nonring D–M–D bond angles (β) change, while in the Rây and Dutt motion those angles (ω) between bonds in the rotating rings change but other nonring angles remain fixed. In the mechanism pictured in Figure 1, the dihedral angle between the planes of the rotating rings always remains 90°, but the nonring angles (ω) between donor–metal bonds in these rings decrease in the transition state.[6]

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[1] P. Rây and N. K. Dutt, *J. Indian Chem. Soc.*, **20**, 81 (1943).

[2] J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.*, **8**, 165 (1958). This mechanism was also proposed independently by W. G. Gehman (Ph.D. Thesis, Pennsylvania State University, State College, Pa., 1954), and L. Seiden (Ph.D. Thesis, Northwestern University, Evanston, Ill., 1957).

[3] T. S. Piper, *J. Am. Chem. Soc.*, **83**, 3908 (1961).

[4] J. I. Legg and B. E. Douglas, *ibid.*, **88**, 2697 (1966).

[5] It is interesting to note that the first three-dimensional X-ray data (R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **5**, 411 (1966)) on a trigonal prismatic compound, $Re(S_2C_2(C_6H_5)_2)_3$, reveal chelate ring angles (*i.e.*, α) of 81.9, 81.5, and 80.9°, in remarkably close agreement with the value calculated by Bailar[2] for the trigonal prismatic transition state having equal D–M–D bond angles. The value originally given was 81° 10′; more refined calculations yield the value 81° 48′.

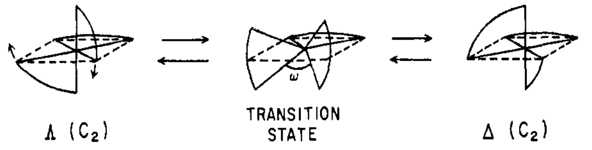

Figure 1.—The intramolecular mechanism proposed by Rây and Dutt for optical isomerization of a tris octahedral complex with bidentate ligands.

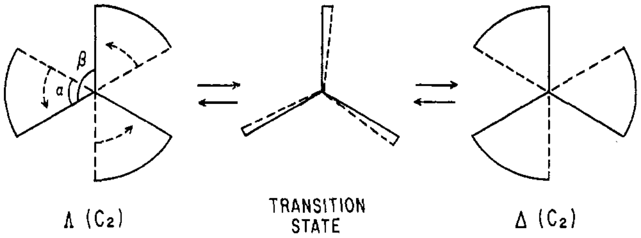

Figure 2.—The intramolecular mechanism proposed by Bailar for optical isomerization of a tris octahedral complex with bidentate ligands as viewed along the C_3 axis.

We wish to propose a new mechanism for intramolecular reorganizations, the motion of which is shown in Figure 3 for the same tris molecule. In this twist, as in the Rây and Dutt mechanism, one ring is imagined to be fixed in space while the other two move. Unlike the Rây and Dutt mechanism, however, the two rings do not rotate past each other in their own planes, but rather revolve past each other while continually changing planes. It is useful from a conceptual standpoint to imagine the two front faces of the octahedron rotating 120° simultaneously but independently about axes passing perpendicularly through their respective face centers. For the absolute configuration shown, the rings can revolve only in the direction indicated. If they were to move in the opposite direction, the Rây and Dutt motion (Figure 1) would be expected to be energetically much more favorable. In this new mechanism, as in that of Rây and Dutt, the chelate ring internal angles remain constant during the transformation. Consequently, the D–M–D angles between bonds in different rings are compressed in the transition state. This mechanism, like both of the other mechanisms, produces optical inversion of the tris molecule.

If one considers any octahedral complex, ignoring the existence of rings and differences in kinds of donor atoms, its structure can be treated as if it had the symmetry of an octahedron or of a complex of composition MA_6. Such compounds have four C_3 axes, about each of which a Bailar twist can occur. Thus, the twist mechanism can be regarded as the motion of the donor atoms around the central metal ion. If one observes the various mechanisms with a model of an MA_6 complex carefully constructed to twist around a C_3 axis, some striking similarities and interrelations will be noted. Keeping a pair of adjacent donor–metal bonds fixed in space, and observing the other two pairs of adjacent bonds, one can see that as the Bailar twist is executed, the two pairs of moving bonds trace out the same general motions described by the twists in Figure 1 or 3 depending upon which set of pairs attention is focused. Since there are four moving bonds, there are two possible sets of pairs of adjacent bonds, each set consisting of two pairs. This is most readily perceived in the tris bidentate case, since, when a chelate ring spans the fixed pair of bonds, there are two possible ways of adding the remaining two rings.

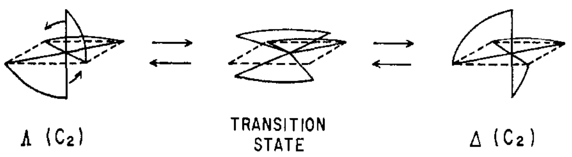

Figure 3.—A proposed intramolecular mechanism for optical isomerization of a tris bidentate octahedral complex.

The introduction of chelate rings and/or different kinds of donor atoms eliminates some or all of the C_3 axes. However, consideration of the twist mechanism as the motions of the donor atoms around the central metal ion will allow the Bailar twist to be performed about each and every C_3 axis or imaginary C_3 axis[7] of any complex molecule with an octahedral array of donor atoms about the central atom. It is clear that Bailar intended that all of the axes be considered because one of the first examples of the mechanism he proposed depicted the ion *cis*-$[Co(en)_2XY]^{n+}$, which has no real C_3 axis.[2] The only *a priori* restriction which must be invoked in considering the Bailar twist is that chelate rings may not ordinarily span *trans* positions.

Examination of the Rây and Dutt twist and the twist presented in this paper reveals that they are actually special cases of the more general Bailar twist. The differences, as pointed out above, lie in the fact that in the special cases particular D–M–D bond angles remain rigid throughout the transition while in Bailar's motion all angles can change. The Rây and Dutt twist is a special case of the Bailar twist about an imaginary C_3 axis because it produces a symmetrically similar transition state while the twist presented in this paper produces a transition state similar to that of the Bailar twist about a real C_3 axis. In general, the transition states generated by the two types of Bailar twist will be

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(6) R. C. Fay and T. S. Piper, *Inorg. Chem.*, **3**, 348 (1964). Calculations reported here showed that a minimum in the electrostatic repulsion of the donor atoms occurs when the dihedral angle between the planes of the rotating rings is expanded from 90 to 115°. This of course will make ω larger in the transition state but will decrease the other nonring D–M–D bond angles (*i.e.*, between the rotating rings and the fixed ring). This argument does not take into account the steric crowding that might be incurred by such an expansion.

(7) An imaginary C_3 axis is here defined as any one of the octahedral face axes (excluding the real C_3 or pseudo C_3 axis) that would be of C_3 symmetry if all rings and differences in donor atoms are disregarded (*i.e.*, consideration of only the octahedral MA_6 coordination cluster). An "imaginary C_3 axis" should not be confused with the "pseudo C_3 axis" employed by Piper, *et al.*,[6,8,9] to designate an axis which would have C_3 symmetry if all rings are regarded as being symmetrical.

(8) R. A. Palmer, R. C. Fay, and T. S. Piper, *Inorg. Chem.*, **3**, 875 (1964).

(9) R. G. Denning and T. S. Piper, *ibid.*, **5**, 1056 (1966).

different.[10] Indeed, it is this difference which accounts for the alternate fates of geometrical isomers.

An example might help to show the generality of these mechanisms. Consider the *cis* isomer of a tris octahedral complex containing unsymmetrical bidentate ligands. This molecule has one C_3 axis and three imaginary C_3 axes. The isomer of chirality Δ (C_2) is shown in Figure 4, with unsymmetrical ligands depicted. The Bailar twist around the real C_3 axis is shown in Figure 4a. As is evident, this mechanism results only in optical inversion but not geometrical isomerization. The twist presented in this paper, when the rings span the donor pairs whose D–M–D angles remain fixed, is the rigid-ring analog of the Bailar twist about the real C_3 axis and is shown in Figure 4b. The similarity of the transition state with respect to the orientations of the rings is apparent; consequently, the new twist results in only optical inversion without the accompanying formation of the *trans* isomer. In Figure 4c is shown the Bailar twist about one of the imaginary C_3 axes which produces simultaneous optical and geometrical isomerization. For this twist the rigid-ring analog is the Rây and Dutt mechanism, shown in Figure 4d. Again, the similarity of the transition states can be noted.

It is important to recognize that the Bailar twist cannot be ruled out by evidence that optical isomerization is accompanied by geometrical isomerization, because optical or both optical and geometrical isomerizations can be effected depending on the particular axis or axes about which the twist is performed. With unsymmetrical ligands the Rây and Dutt twist and the Bailar twist about an imaginary C_3 axis can give simultaneous optical and geometrical isomerization. On the other hand, nuclear magnetic resonance data or stereochemical evidence of the type described by Fay and Piper[6] can be used to rule out the new mechanism and the Bailar twist about a real C_3 axis as the sole pathway since there are no circumstances in which they convert *cis* to *trans*.

Conclusions

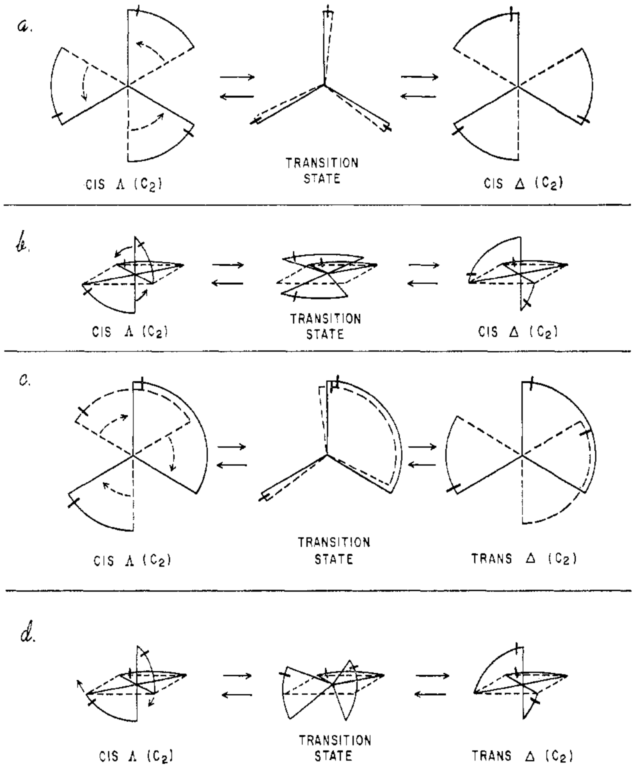

Figure 4.—a. The Bailar twist about the C_3 axis of a tris complex with unsymmetrical bidentate ligands as viewed along the C_3 axis. b. The rigid-ring analog of the Bailar twist about the C_3 axis of a tris complex with unsymmetrical bidentate ligands. c. The Bailar twist about an imaginary C_3 axis of a tris complex with unsymmetrical bidentate ligands as viewed along the axis of rotation. d. The Rây and Dutt rigid-ring analog of the Bailar twist about an imaginary C_3 axis of a tris complex with unsymmetrical bidentate ligands.

The Bailar twist has been shown to be a very general intramolecular nonbond rupture mechanism which can account for both optical and geometrical isomerization of octahedral complexes. For chelate complexes the Rây and Dutt mechanism and the mechanism introduced herein have been shown to be special cases of the Bailar twist where the rings remain rigid throughout the transformation. Any actual intramolecular isomerization mechanism not involving bond rupture in all likelihood lies somewhere between the ideal Bailar mechanism, which would have all D–M–D bond angles equal to 81° 48′ in the transition state, and the rigid-ring cases, which would have ring D–M–D bond angles of approximately 90° in the transition state. However, it should be recognized that in extreme cases of steric crowding between chelate rings, the ring D–M–D bond angles may be forced to even smaller values than 81° 48′. It would seem that in chelate molecules with particularly rigid rings the fixed-ring mechanisms might be preferred, while those with less rigid ligands or with particularly bulky substituents might follow the more flexing Bailar pathway. Finally, the activation energies for the rigid- and flexing-ring cases, though probably of similar values, must be different. Energy may be either released or expended in flexing the rings, and the ligand electrostatic repulsion energy must be different for the two possible shapes of transition states.

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[10] Fay and Piper[6] have coined the terms "trigonal twist" and "rhombic twist" for tris octahedral complexes with bidentate ligands. A twist is termed "trigonal" if it produces a transition state which has a C_3 or pseudo C_3 axis. A "rhombic" twist, on the other hand, generates a transition state which has neither of these elements of symmetry. It is shown in Figure 4a and c that a Bailar twist can produce either a "trigonal" or a "rhombic" transition state depending upon the axis about which the molecule rotates.