one of the possible isomers by preferentially occupying the less sterically hindered sites is also noted in five-coordinate complexes.[8]

(8) D. L. Kepert, *Inorg. Chem.*, 12, 1938 (1973).

It can also be predicted that unidentate ligands which form progressively weaker bonds with the metal atom will progressively stabilize stereochemistry A as it approaches the distorted[2] octahedral M(bidentate)$_3$.

# Notes

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## Solvent-Assisted Racemization of Tris-Chelate Complexes

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Rearrangements of six-coordinate tris-chelate complexes are usually envisaged as occurring through five-coordinate intermediates by bond rupture, or through various intramolecular twist mechanisms.[1] A third possible mechanism examined here is the entry, or partial entry, of a solvent molecule as a unidentate ligand to form a seven-coordinate complex with a much lower activation energy for intramolecular rearrangement.

unidentate ligand bond length and the metal–donor atom bond length for the bidentate ligands. That is, M–A $= Rr$.

### Results and Discussion

Two mechanisms need be considered for the racemization of M(bidentate)$_3$(unidentate) complexes of stereochemistry A[2] (the capped trigonal antiprism), formed by introducing a solvent molecule into the coordination sphere of a tris-bidentate complex.

The first is the twisting of all three bidentate ligands in the same direction about the respective metal–bidentate ligand axes, leading to a transition state which is a trigonal prism formed from three approximately parallel bidentate ligands with the unidentate ligand capping one of the triangular faces, $C_3$ symmetry being retained throughout. It is always found that the activation energy for this triple twisting is greater than for the corresponding process in the absence of unident-
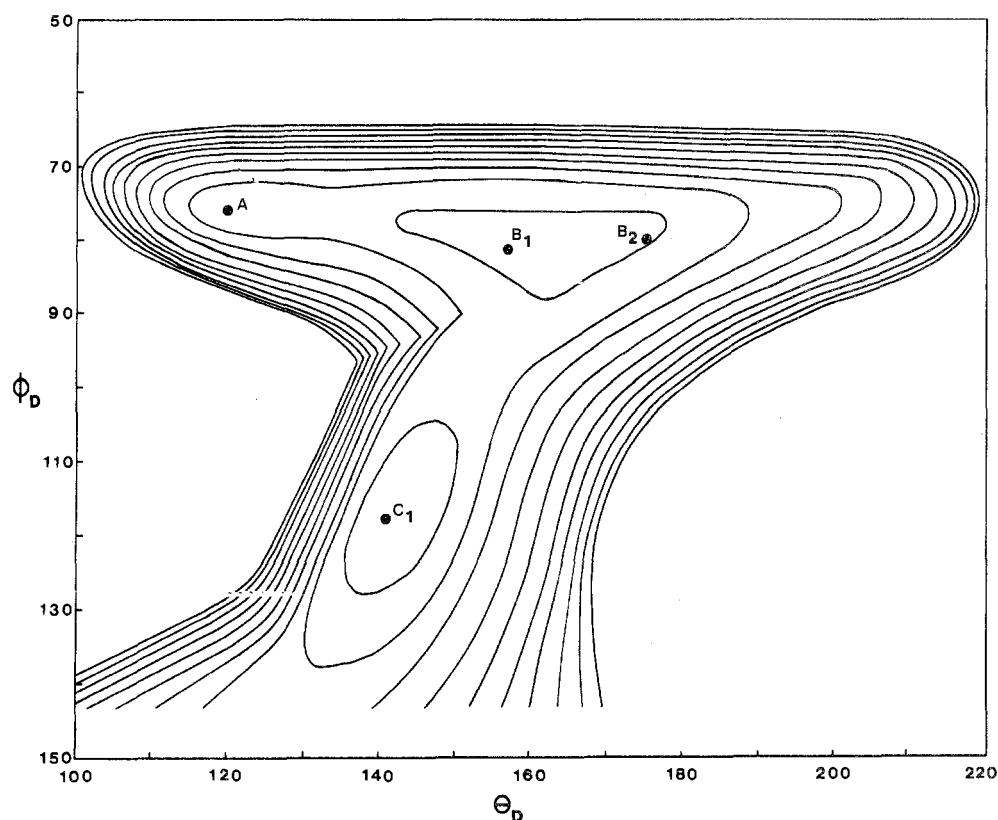


**Figure 1.** Potential energy surface for the racemization of M(bidentate)$_3$(unidentate); $R = 1.00$, $b = 1.2$, $n = 6$. The repulsion energies have been normalized so that successive contours are for 1% energy increases above the bottom of the potential energy surface at stereochemistry B$_1$.

### Method

The repulsion energy coefficients were calculated as before,[2] with the additional variable $R$, the ratio between the metal–

ate ligand,[3] namely, the twisting around a real or pseudo $C_3$ axis, operation A$_6$ of ref 1, or the "Bailar twist."

The second mechanism is most simply visualized as being initiated by the twisting of two of the bidentate ligands (for

(1) S. S. Eaton and G. R. Eaton, *J. Amer. Chem. Soc.*, 95, 1825 (1973), and references therein.
(2) D. L. Kepert, *Inorg. Chem.*, 13, 2754 (1974).

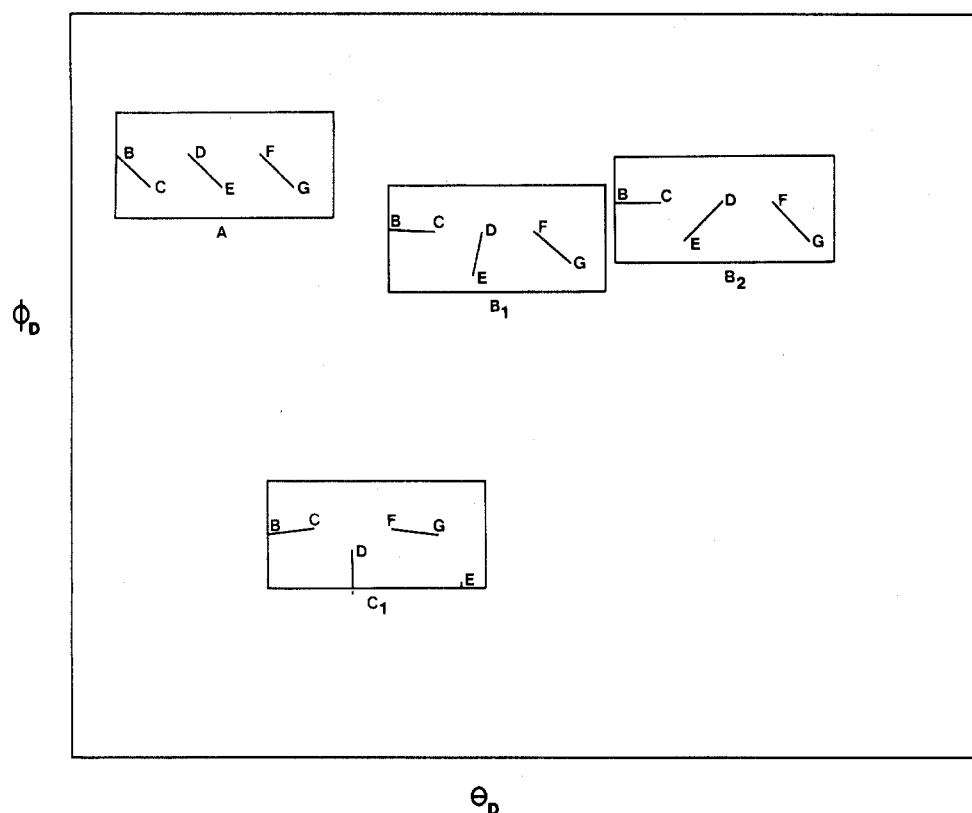(3) D. L. Kepert, *Inorg. Chem.*, 11, 1561 (1972).

**Figure 2.** Mercator projections of the four stereochemistries noted in Figure 1. In all cases the unidentate at $\phi = 0°$ is not shown.
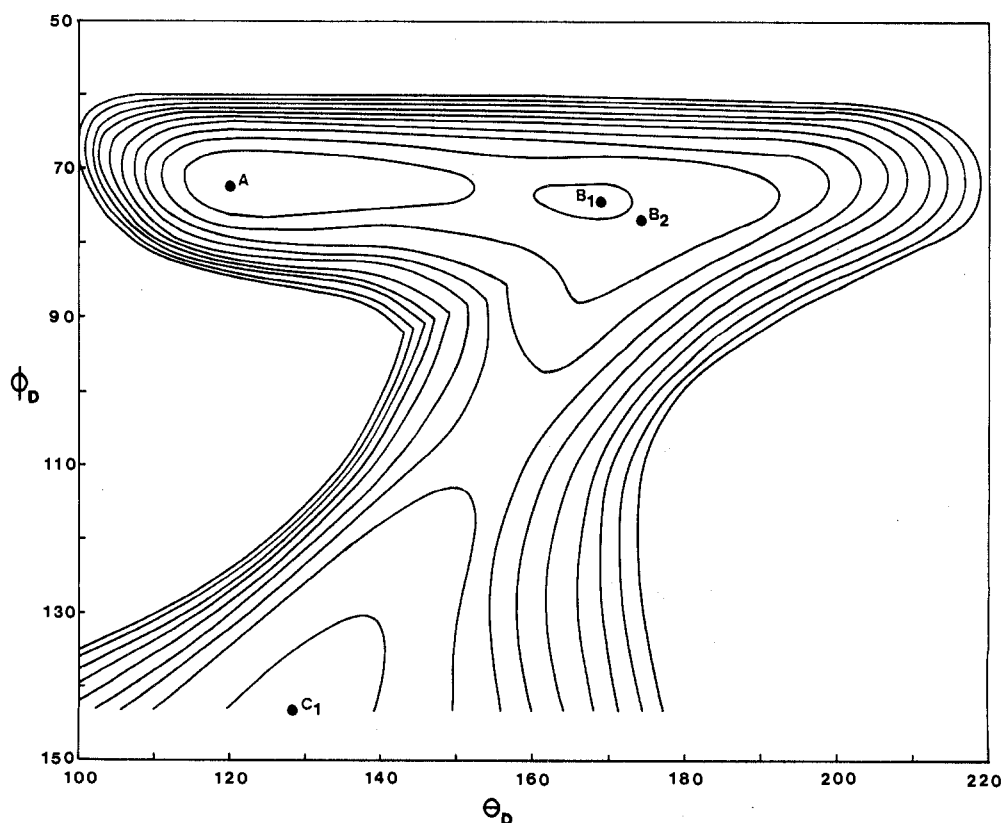


**Figure 3.** Potential energy surface for the racemization of M(bidentate)$_3$(unidentate); $R = 1.20$, $b = 1.2$, $n = 6$. The repulsion energies have been normalized so that successive contours are for 1% energy increases above the bottom of the potential energy surface at stereochemistry A.

example BC and DE; see Figure 2) in *opposite* directions about their respective metal–bidentate ligand axes. A typical potential energy surface calculated with all bond lengths equal is shown in Figure 1, projected onto the polar coordinates of atom D which most clearly separates the minima due to the different stereochemistries. To prevent overlapping
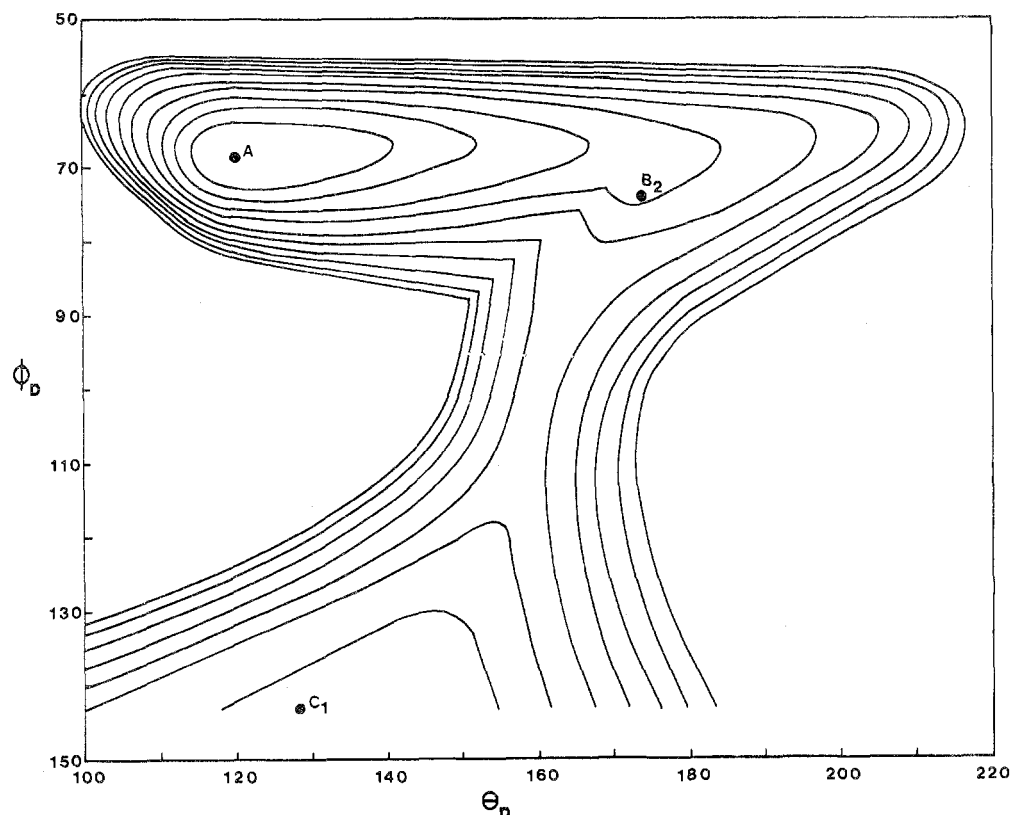
**Figure 4.** Potential energy surface for the racemization of M(bidentate)$_3$(unidentate); $R = 1.40$, $b = 1.2$, $n = 6$. The repulsion energies have been normalized so that successive contours are for 1% energy increases above the bottom of the potential energy surface at stereochemistry A.

of a large number of minima due merely to an interchange of atom labels and/or the definition of axes, it is also necessary to specify

$$|\phi_D - \phi_E| \geqslant |\phi_F - \phi_G| \geqslant |\phi_B - \phi_C|$$

The apparent cusp near $\phi_D = 90°$ and $\theta_D = 140°$ is due to the overlap of two valleys on the potential energy surface when projected onto this $\phi_D$–$\theta_D$ plane. The valley on the upper part of the figure corresponds to $\phi_C > \phi_D$; the other on the lower part of the Figure, to $\phi_C < \phi_D$. That is, atom D can only readily move past atom C at high values of $\theta_D$.

The associated stereochemistries[2] marked on Figure 1 are viewed as Mercator projections in Figure 2, in each case the unidentate ligand being situated at the "north pole" with $\phi_A = 0°$. Racemization can proceed through stereochemistry $B_2$ or through stereochemistry $C_1$, both of which contain a mirror plane. In all cases the energy of activation is simply taken as the energy required to climb out of the well associated with stereochemistry A, since it is not necessary to descend completely to stereochemistries $B_2$ or $C_1$ to reach a stereochemistry which is optically inactive. This activation energy is very small. For example using a normalized bite for the bidentate ligand of $b = 1.2$ and a repulsive energy exponent of $n = 6$, as in Figure 1, with the repulsive energy coefficient $X$ for stereochemistry A being 2.2874,[2] the activation energy is 0.0030. This is only 2% of the activation energy of 0.125 for the "Bailar twist," or only 0.2% of the activation energy of 1.456 for the seven-coordinate "solvent-hindered Bailar twist."

The effect of increasing the metal–unidentate ligand bond length from $R = 1.0$ to $R = 1.2$ and $R = 1.4$ is shown in Figures 3 and 4, respectively. The general appearances of the potential energy surfaces are not greatly altered, although
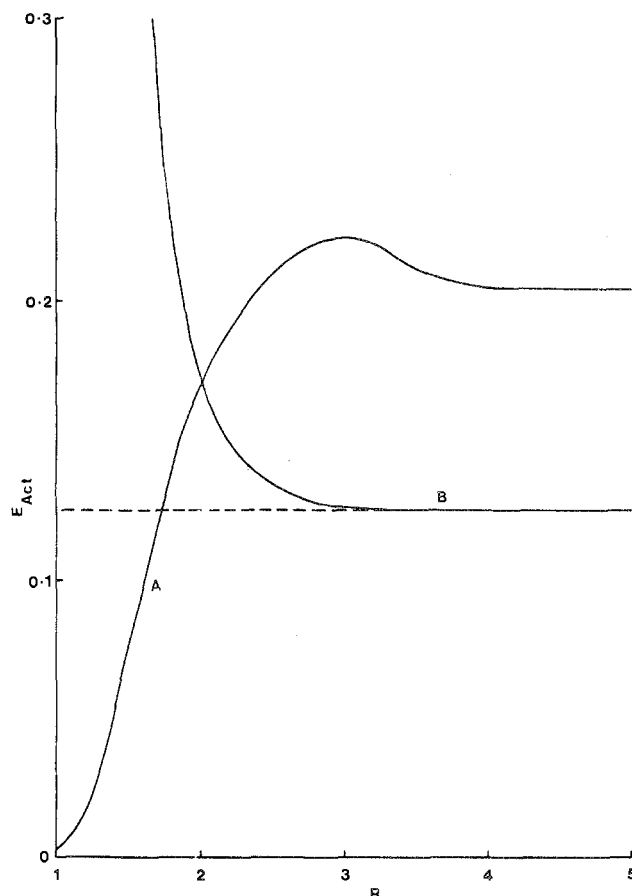


**Figure 5.** Activation energy for racemization of M(bidentate)$_3$-(unidentate) by a double-opposed-initiated twist mechanism (curve A) and a triple-twist mechanism (curve B); $b = 1.2$, $n = 6$.

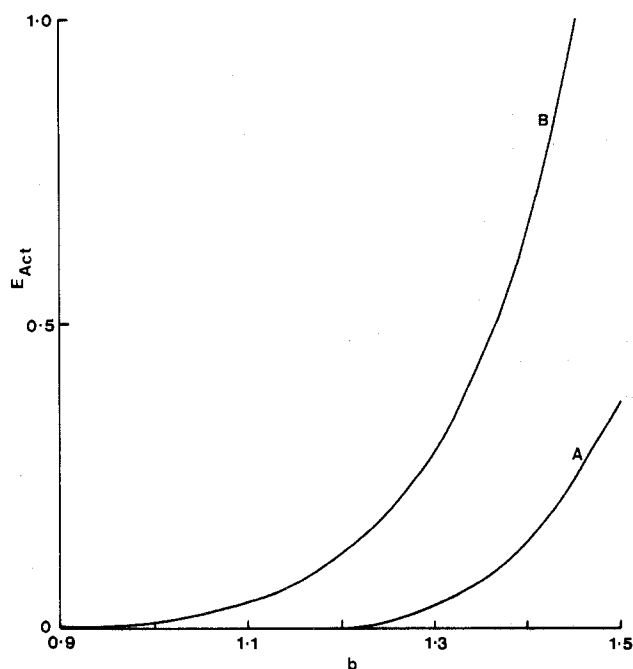**Figure 6.** Activation energy for racemization of M(bidentate)$_3$-(unidentate) by a double-opposed-initiated twist mechanism (curve A), $R = 1.00$, and of M(bidentate)$_3$ by a Bailar twist mechanism (curve B), $n = 6$.

## Characterization of Heptacyanovanadate(III)

Robert A. Levenson,* Richard J. G. Dominguez, Michael A. Willis, and Floyd R. Young, III

The structure of the heptacyanovanadate(III) ion, V(CN)$_7^{4-}$, has been shown to be a pentagonal bipyramid from a single-crystal X-ray crystallographic study of K$_4$V(CN)$_7$·2H$_2$O.[1,2] Although this anion had been prepared in a number of studies,[3-11] its structure, frequently presumed to be octahedral, had never been explicitly determined. The possibility of seven-coordination, however, had indeed been recognized by several groups of workers.[6-11] Since this same material was most likely prepared by Alexander and Gray[7] (although they formulated it as a hexacyanide, their analytical results are essentially perfect for K$_4$V(CN)$_7$·2H$_2$O) and since they reported difficulty in repeating the synthesis, a separate and detailed elaboration of the synthesis and properties of K$_4$V-(CN)$_7$·2H$_2$O appears warranted. Further impetus stems from reports that anhydrous[10] and monohydrated[9] forms of the same material have been prepared. The V(CN)$_7^{4-}$ anion need not necessarily have the same structure in these several compounds in view of the work on the analogous Mo(CN)$_7^{4-}$ complex which indicates that, while in the anhydrous potassium salt and in an aqueous solution the seven-coordinate anion has a pentagonal-bipyramidal structure, monocapped trigonal-prismatic coordination obtains in the dihydrate.[12]

Since the structure of K$_4$V(CN)$_7$·2H$_2$O is now firmly established, we herein report a vibrational study in the cyanide stretching region (infrared and Raman in both the solid state and aqueous cyanide) and an electron spin resonance study of the species present in solution. An emission observed while examining the Raman spectrum is interpreted in terms of a ligand field study which has already been presented;[13] a molecular orbital treatment of this fundamentally interesting species has also been given.[14]

### Experimental Section

it may be noted that the minimum due to stereochemistry C$_1$ moves to higher $\phi_D$ until it corresponds to a capped trigonal prism rather than to a stereochemistry intermediate between a capped trigonal prism and a pentagonal bipyramid.[2] The important feature is that the progressive stabilization of the capped trigonal antiprism as the unidentate ligand is withdrawn is relatively small. In all cases the minimum activation energy for racemization is simply the energy required to climb out of the well of stereochemistry A. Even at $R = 1.4$, which must be considered to be a fairly weak metal–unidentate ligand interaction, the activation energy for this "double-opposed-initiated" twisting is less than half that for the Bailar twist mechanism.

The detailed relation between the value of $R$ and the activation energy for these racemization reactions is shown in Figure 5, which shows that the solvent-assisted double-opposed-initiated twist mechanism is more probable than the solvent-hindered triple-twist mechanism as long as $R < 2.0$. When $R = \infty$, the activated complex of stereochemistry B$_2$ for this double-opposed-initiated twist becomes identical with the activated complex for the Ray and Dutt twist, or twisting around an imaginary C$_3$ axis (operation A$_8$ of ref 1). Similarly the activated complex of stereochemistry C$_1$ becomes identical with the activated complex of the Bailar twist.

The effect of changing the normalized bite $b$ of the bidentate ligand on the activation energies for the solvent-free Bailar twist and the solvent-assisted double-opposed-initiated twist for $R = 1$ is shown in Figure 6. The activation energies for both processes decrease as expected as $b$ is decreased, but for the latter to a greater extent.

These general conclusions are not altered by using values of $n = 1$ or 12 in the assumed repulsive law.

In summary, it is concluded that the mechanism of racemization may change from a triple-twist process to a double-opposed-initiated twist process as the coordinating ability of the solvent increases. These two processes are experimentally distinguishable if asymmetric chelating agents are used.[1]

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(13) R. A. Levenson and R. J. G. Dominguez, *Inorg. Chem.*, **12**, 2342 (1973).

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