lutions have been measured up to 4 m^{17} and [HF] has been evaluated from these data by interpolation and using density data in ref 18. While water activities in aqueous HF solutions have not been measured, values for a_{H_2O} may be obtained from the vapor pressure measurements of Fredenhagen.[19] The validity of this approach has been demonstrated for aqueous HCl solutions where a_{H_2O} values from vapor pressure measurements agree within experimental error with those obtained by emf methods.[20] The effect on a_{H_2O} and [HF] of a relatively small concentration of $HClO_4$ in these solutions has not been taken into consideration but its effect must be small in view of the satisfactory agreement between K_h values for the solutions given in Table II. The hydrolysis constant K_h, was found to be 2.5 ± 0.1 ml^{-1}.

It is interesting that the apical F is replaced in the hydrolysis of TeF_5^-. This behavior parallels that observed for substitution reactions with IF_5 where the apical F is readily replaced by OMe[21] and OH.[22] The apical fluorine is more strongly bonded to the central atom than the basal fluorines are, judging from their respective bond distances.[23,24] It would appear that the facile displacement of the apical fluorine may arise from the ease of attack at the trans position. Secondary bonding in several fluorine-containing solids such as $XeF_2 \cdot IF_5$ has been observed to take place at this position.[25]

Acknowledgment. We thank the National Research Council of Canada for financial support. We are very grateful to Dr. A. R. Davis for the use of his Raman spectrometer.

Registry No. $KTe(OH)F_4$, 52279-46-6; $KTeF_5$, 52279-47-7; $Te(OH)F_4^-$, 52279-48-8; TeF_5^-, 37419-76-4; HF, 7664-39-3.

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Stereochemistry of Seven-Coordinate Complexes Containing Three Bidentate Ligands

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Received February 13, 1974 AIC40101K

Minimization of the repulsive energy around a seven-coordinate metal atom bonded to three rigid chelating bidentate ligands shows that three separate minima occur on the potential energy surfaces. These correspond respectively to the capped octahedron with the unidentate ligand lying on the threefold axis, a very irregular stereochemistry containing no elements of symmetry, and a stereochemistry intermediate between a pentagonal bipyramid and a capped trigonal prism, with the unidentate ligand lying on a mirror plane. These predictions are in agreement with known crystal structures. Factors which may favor particular stereochemistries are briefly discussed.

The stereochemistry of complexes resulting from the introduction of bidentate ligands into the coordination sphere is often significantly different from the stereochemistry of complexes containing only unidentate ligands and cannot be calculated from considerations of metal-ligand bonding. The stereochemistry can, however, be determined with remarkable accuracy and simplicity by minimization of the total "ligand-ligand repulsion energy" or, alternatively, the equivalent bond-bond repulsion energy. Investigations into five-,[1] six-,[2,3] seven-,[4] and eight-coordinate[5] complexes is now continued with the seven-coordinate M(bidentate)$_3$(unidentate) complexes. Some comments on the stereochemistry of lanthanoid shift reagents of this stoichiometry have been made elsewhere.[6]

Method

The position of the unidentate ligand A and of each end of the bidentate ligands BC, DE, and FG on the surface of a sphere of radius r about the metal atom is defined by the spherical coordinates ϕ_i and θ_i. The axes are defined by placing the unidentate ligand A at the "north pole," with $\phi_A = 0°$, and the donor atom B at "zero longitude," $\theta_B = 0°$. The coordinates of the i atom are given by the "latitude" ϕ_i, which is defined as the angle between the metal-ligand M-i bond and the axis incorporating the metal-ligand bond M-A. The "longitude" θ_i is defined as the angle between the vertical plane incorporating MAB and the vertical plane incorporating MAi.

The distance between any two such ligand sites i and j is given by

$$d_{ij} = [2 - 2 \cos \phi_i \cos \phi_j - 2 \sin \phi_i \sin \phi_j \cos (\theta_i - \theta_j)]^{1/2} r$$

For any general bidentate PQ, the coordinate ϕ_Q was calculated from $\phi_P, \theta_P, \theta_Q$, and the "normalized bite" b of the chelate, which is defined as the distance between the two donor atoms of the chelate divided by the metal-ligand bond length, *i.e.*

$$b = d_{PQ}/r$$

It is again assumed that the repulsive energy u_{ij} between

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Table I. Structural Parameters for Stereochemistry A[a]

		Angles, deg			
b	n	ϕ_B	ϕ_C	θ_C	X
0.8	1	82.2	121.6	27.1	11.3823
	6	85.2	122.3	30.6	1.4139
	12	86.6	123.3	31.4	0.1556
0.9	1	80.3	123.2	33.6	11.5056
	6	82.9	124.1	36.1	1.5742
	12	84.2	125.1	36.6	0.2018
1.0	1	78.4	124.7	40.3	11.6447
	6	80.5	125.8	41.8	1.7694
	12	81.8	126.9	42.3	0.2655
1.1	1	76.4	126.2	47.1	11.7995
	6	78.3	127.5	48.1	2.0052
	12	79.5	128.7	48.5	0.3534
1.2	1	74.6	127.7	54.6	11.9693
	6	76.1	129.2	55.0	2.2874
	12	77.2	130.4	55.2	0.4741
1.3	1	72.8	129.2	62.5	12.1527
	6	74.0	130.8	62.6	2.6206
	12	75.0	132.0	62.8	0.6385
1.4	1	71.1	130.6	71.3	12.3466
	6	72.0	132.3	71.1	3.0049
	12	73.0	133.5	71.4	0.8571
1.5	1	69.6	131.9	81.1	12.5457
	6	70.2	133.7	80.8	3.4309
	12	71.1	134.9	81.1	1.1349

[a] $\phi_D = \phi_F = \phi_B$, $\phi_E = \phi_G = \phi_C$, $\theta_D = 120$, $\theta_E = \theta_D + \theta_C$, $\theta_F = 240$, $\theta_G = \theta_F + \theta_C$.

any two donor atoms i and j is proportional to some inverse power n of the distance between them. The value of n is not known, but the best agreement with experiment appears to be with values in the range 6-10. In this work, the previous custom of using $n = 1$ (a coulombic repulsion), 6, and 12 is continued. The total repulsion energy U is then

$$U = \sum_{ij} u_{ij} = \sum_{ij} a d_{ij}^{-n} = aX_r^{-n}$$

where a is the proportionality constant and X is the repulsion energy coefficient calculated from the value of n and the geometry of the coordination polyhedron.

Each chelated ligand is again assumed to be sufficiently rigid that the interaction between its two donor atoms can be regarded as constant and can therefore be neglected when comparing different stereochemistries.

The repulsion energy coefficient X was calculated as a function of ϕ_B, θ_C, ϕ_D, θ_D, θ_E, ϕ_F, θ_F, and θ_G. The location of each minimum was determined to the nearest 0.1° in each of the angular coordinates.

Results

There are a large number of stereochemistries which can be envisaged for seven-coordinate complexes of the type M(bidentate)$_3$(unidentate), but in general only three separate minima corresponding to three separate groups of stereochemistries are observed on each potential energy surface.

Group A. Isomer A contains a threefold axis and corresponds to the capped trigonal antiprism (Figure 1). Angular parameters and values for the repulsion coefficient X are given in Table I.

Group B. The potential energy minimum corresponding to group B is very shallow, the precise stereochemistry at the minimum depending upon the values of b and n. Over most of the range of b and n the stereochemistry, denoted as stereochemistry B$_1$, has no elements of symmetry and the solid chosen to describe best the conventional coordination polyhedron is somewhat arbitary; for example see Figure 1. Angular parameters and values for the repulsion coefficient X are given in Table II.

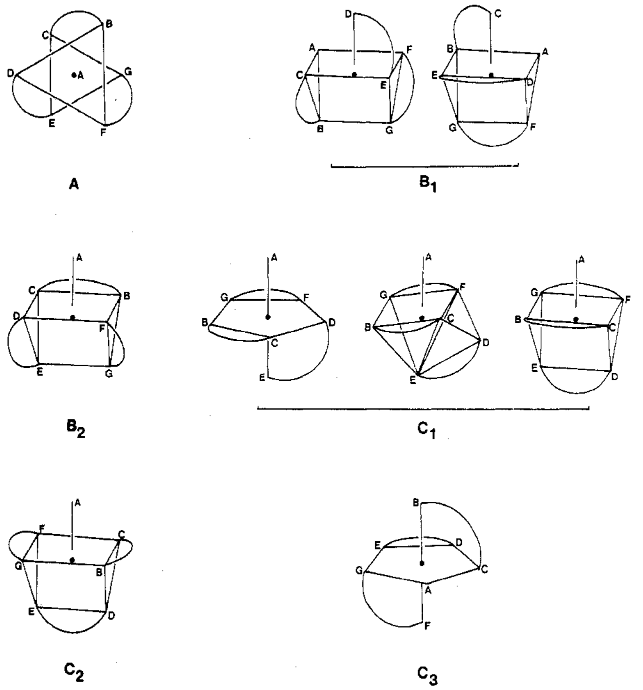

Figure 1. Stereochemistries of M(bidentate)$_3$(unidentate) complexes.

At very low values of b for $n = 1$ and 6 and for very high values of b for $n = 12$, it is observed that $\phi_B = \phi_C$, $\phi_D = \phi_F$, $\phi_E = \phi_G$, and the stereochemistry corresponding to minimum energy, now denoted as B$_2$, contains a mirror plane (Figure 1 and Table III).

Group C. The third minimum on the potential energy surface is also very shallow. In most cases the stereochemistry contains a mirror plane (stereochemistry C$_1$, Figure 1, Table IV), and is intermediate between a pentagonal bipyramid with $\phi_B = \phi_C = \phi_D$ and a capped trigonal prism with $\phi_B = \phi_C$ and $\phi_E = 360 - \phi_D$ (since the convention used in Table IV allows ϕ_E to go above 180°, retaining $\theta_E = \theta_D$). This potential energy minimum is particularly shallow in the direction of increasing ϕ_D and ϕ_E, which is also reflected in the relatively large differences calculated for $n = 1$, 6, and 12. Although the BCDFG plane of the pentagonal plane is always puckered to some extent, that is $\phi_B \neq \phi_C \neq \phi_D$, the pentagonal bipyramid is a reasonable description of the structure for $b \leqslant 1.1$. As the normalized bite increases, the bidentate ligand DE progressively swings around in the direction required for the formation of the capped trigonal prism. However this limiting stereochemistry is only reached when $n = 12$ and $b = 1.4$; in other cases this minimum is taken over by other minima, C$_2$ or C$_3$ (see below). If a mirror plane is artificially imposed so as to prevent the formation of stereochemistries C$_2$ and C$_3$, stereochemistry C$_1$ becomes identical with that of the capped trigonal prism at $b \geqslant 1.42$ (for $n = 1$) and $b > 1.34$ (for $n = 6$ and 12). It has been pointed out elsewhere[7] that this rotation is clearly shown in the isomorphous [NbO(S$_2$CNEt$_2$)$_3$] and [VO(S$_2$CNEt$_2$)$_3$], where the increase in mean normalized bite from $b = 1.108$ to $b = 1.128$ is accompanied by an increase in ϕ_D from 95.1 to 97.6° and an increase in ϕ_E from 161.3 to 166.2°.

As b becomes very large, the capped rectangular face BCFG changes from one in which the bidentate ligands span

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Table II. Structural Parameters for Stereochemistry B_1

		Angles, deg											
b	n	ϕ_B	ϕ_C	θ_C	ϕ_D	θ_D	ϕ_E	θ_E	ϕ_F	θ_F	ϕ_G	θ_G	X
0.8	12	90.3	93.1	47.1	91.3	142.1	138.4	139.9	88.1	236.8	120.1	273.1	0.1461
0.9	6	88.0	91.2	53.4	88.0	148.0	141.1	140.4	84.9	241.6	124.8	279.5	1.5443
	12	88.1	91.3	53.4	90.5	143.6	144.0	141.2	86.1	233.6	119.4	277.3	0.1859
1.0	6	86.1	89.0	60.0	88.7	148.6	148.3	140.1	82.9	236.4	122.2	284.0	1.7293
	12	86.1	89.0	60.0	89.1	146.0	149.0	140.7	84.2	231.7	120.1	281.9	0.2426
1.1	1	81.6	89.2	66.6	81.4	160.5	146.2	141.1	81.2	249.8	133.2	295.9	11.7905
	6	82.1	89.3	66.6	85.4	152.0	151.6	141.6	81.7	236.8	124.5	291.0	1.9633
	12	82.5	87.9	66.8	85.2	150.0	151.5	140.0	82.5	233.0	123.7	288.5	0.3285
1.2	1	76.6	93.0	72.5	78.8	159.6	152.2	150.1	81.3	246.4	130.8	306.0	11.9636
	6	78.3	88.5	73.7	81.3	157.0	154.0	140.4	80.7	239.3	128.1	300.0	2.2641
	12	79.1	85.4	74.3	81.4	156.1	153.1	133.6	80.3	237.1	128.5	297.2	0.4604
1.3	1	71.2	104.0	75.3	73.4	152.5	152.4	175.8	80.8	244.5	128.9	315.1	12.1528
	12	76.6	79.2	83.3	78.7	166.4	150.7	118.6	77.1	245.7	135.0	308.7	0.6614
1.4	6	71.6	78.6	92.6	70.8	202.5	142.3	141.5	89.3	276.8	142.6	364.0	3.1359
1.5	6	68.7	79.2	102.2	67.9	202.5	150.2	138.5	82.8	276.9	136.0	369.8	3.7253

Table III. Structural Parameters for Stereochemistry B_2[a]

		Angles, deg						
b	n	ϕ_B	θ_C	ϕ_D	θ_D	ϕ_E	θ_E	X
0.8	1	92.2	47.2	84.5	152.1	129.5	136.8	11.3792
	6	91.5	47.2	87.3	154.2	131.2	135.4	1.3940
0.9	1	89.8	53.5	83.2	157.4	133.3	136.8	11.4991
1.0	1	87.3	60.1	82.0	163.1	137.0	136.0	11.6358
1.4	12	74.1	93.4	74.9	187.5	143.1	120.7	0.9652
1.5	12	71.2	104.8	73.0	194.8	141.0	114.6	1.4334

[a] $\phi_C = \phi_B, \phi_F = \phi_D, \theta_F = 360 + \theta_C - \theta_D, \phi_G = \phi_E, \theta_G = 360 + \theta_C - \theta_E$.

Table IV. Structural Parameters for Stereochemistry C_1[a]

		Angles, deg						
b	n	ϕ_B	ϕ_C	θ_C	ϕ_D	θ_D	ϕ_E	X
0.8	1	104.1	86.7	44.2	97.5	136.0	144.7	1.4010
	6	103.0	87.8	45.0	99.7	135.2	146.9	0.1467
0.9	1	103.6	81.6	49.1	96.1	138.9	149.6	11.5079
	6	100.9	85.0	51.3	100.5	137.7	154.0	1.5452
	12	99.7	86.0	51.9	103.9	137.0	157.4	0.1853
1.0	1	99.6	80.7	57.2	100.1	140.3	160.1	11.6411
	6	97.5	83.5	58.5	104.7	139.1	164.7	1.7208
	12	94.7	84.4	59.2	111.2	138.7	171.2	0.2405
1.1	1	95.1	80.2	65.3	105.4	141.2	172.1	11.7896
	6	93.5	81.9	65.9	110.0	140.4	176.7	1.9470
	12	90.0	82.2	66.5	118.0	139.8	184.7	0.3253
1.2	1	90.4	79.9	73.4	112.0	141.4	185.7	11.9604
	6	88.2	80.0	73.8	117.6	140.9	191.3	2.2539
	12	84.7	79.8	74.4	124.9	140.0	198.6	0.4581
1.3	1	86.9	79.5	81.5	117.7	141.5	198.8	12.1671
	6	81.2	77.8	82.7	128.8	138.6	209.9	2.6706
	12	79.2	77.2	83.2	131.3	138.7	212.4	0.6654
1.4	12	75.1	75.2	92.8	135.6	136.4	224.5	1.0018

[a] $\theta_E = \theta_D, \phi_F = \phi_C, \theta_F = 2\theta_D - \theta_C, \phi_G = \phi_B, \theta_G = 2\theta_D$.

Table V. Structural Parameters for Stereochemistry C_2[a]

		Angles, deg			
b	n	ϕ_B	θ_C	ϕ_D	X
1.2	12	75.4	76.6	143.1	0.7373
1.3	6	75.5	84.3	139.5	2.9279
	12	74.9	84.6	139.5	0.8147
1.4	6	75.6	92.6	135.6	3.1287
	12	74.8	93.0	135.6	0.8990
1.5	6	76.6	100.9	131.4	3.3959
	12	75.6	101.5	131.4	1.0367

[a] $\phi_C = \phi_F = \phi_G = \phi_B, \theta_D = \theta_C/2, \phi_E = 360 - \phi_D, \theta_E = \theta_D, \theta_F = 180, \theta_G = \theta_F + \theta_C$.

Table VI. Structural Parameters for Stereochemistry C_3[a]

		Angles, deg				
b	n	ϕ_B	ϕ_C	θ_C	ϕ_D	θ_D	X
1.3	1	88.6	72.9	81.1	139.5	109.3	12.1621
1.4	1	89.9	67.4	88.8	135.6	93.0	12.3717
1.5	1	97.2	66.2	94.7	131.4	83.1	12.5568

[a] $\phi_E = \phi_D, \theta_E = 180 + \theta_D, \phi_F = \phi_B, \theta_F = 180, \phi_G = \phi_C, \theta_G = \theta_F + \theta_C$.

Table VII. Repulsion Coefficients X Normalized to Those of Stereochemistry A

b	A	B_1	B_2	C_1	C_2	C_3
			$n = 1$			
0.8	1.0000		0.9997			
0.9	1.0000		0.9994	1.0002		
1.0	1.0000		0.9992	0.9997		
1.1	1.0000	0.9992		0.9992		
1.2	1.0000	0.9995		0.9993		
1.3	1.0000	1.0000		1.0012		1.0008
1.4	1.0000					1.0020
1.5	1.0000					1.0009
			$n = 6$			
0.8	1.000		0.986	0.991		
0.9	1.000	0.981		0.982		
1.0	1.000	0.977		0.973		
1.1	1.000	0.979		0.971		
1.2	1.000	0.990		0.985		
1.3	1.000			1.019	1.117	
1.4	1.000	1.044			1.041	
1.5	1.000	1.086			0.990	
			$n = 12$			
0.8	1.000	0.939		0.943		
0.9	1.000	0.921		0.918		
1.0	1.000	0.914		0.906		
1.1	1.000	0.930		0.921		
1.2	1.000	0.971		0.966	1.555	
1.3	1.000	1.036		1.042	1.276	
1.4	1.000		1.126	1.169	1.049	
1.5	1.000		1.263		0.913	

the opposite short edges to one in which the bidentate ligands span the opposite long edges. For $n = 6$ and 12, the stereochemistry C_1, which has the projection of the third bidentate ligand DE pointing between the other two bidentate ligands, becomes destabilized relative to the capped trigonal prism C_2 in which the projection of DE is pointed at the other two bidentate ligands (Figure 1, Table V). There is a significant potential energy barrier between stereochemistries C_1 and C_2, particularly for $n = 12$ where it is more difficult for the atoms to push past each other, and both stereochemistries may occur as minima. As b becomes very large for the case of $n = 1$, the projection of this DE bidentate ligand is intermediate between that observed for stereochemistries C_1 and C_2, and this stereochemistry C_3 is best represented as a pentagonal bipyramid (Figure 1, Table VI).

Table VIII. Stereochemistry of $M(bidentate)_3(unidentate)$ Complexes

Stereochemistry A	*b*	ϕ_{BDF}, deg	Ref
$[Ho(PhCOCHCOPh)_3(H_2O)]$	1.21	74	*a*
$[Y(PhCOCHCOMe)_3(H_2O)]$	1.21	75	*b*
$[W(PhC{\equiv}CPh)_3(CO)]$	0.62	86	*c*

Stereochemistry B_1	*b*	ϕ_{BCDF}, deg	Ref
$[Yb(MeCOCHCOMe)_3(MeCOCH{=}C(NH_2)Me)]$	1.23	84	*d*
$[Dy(t\text{-}BuCOCHCO\text{-}t\text{-}Bu)_3(H_2O)]$	1.20	84	*e*
$[Lu(C_3F_7COCHCO\text{-}t\text{-}Bu)_3(H_2O)]$	1.23	83	*f*
	1.22	83	*f*
$[Yb(MeCOCHCOMe)_3(H_2O)]$	1.23	80	*g*
	1.25	79	*g*
$[Yb(MeCOCHCOMe)_3(H_2O)]\cdot{}^1/_2C_6H_6$	1.22	79	*h*
$[Lu(t\text{-}BuCOCHCO\text{-}t\text{-}Bu)_3(MeC_5H_4N)]$	1.22	86	*i*
$[Eu(t\text{-}BuCOCHCO\text{-}t\text{-}Bu)_3(OS(CH_2)_2CMe_2)]$			*j*

Stereochemistry C_1	*b*	ϕ_{BCFG}, deg	Ref
$[Zr(MeCOCHCOMe)_3Cl]$	1.24	89	*k*
$[Sn(C_7H_5O_2)_3Cl]$	1.20	91	*l*
$[Sn(C_7H_5O_2)_3(OH)]$	1.19	92	*l*
$(NH_4)_3[Nb(C_2O_4)_3O]\cdot H_2O$	1.19	96	*m*
$A_3[Sb(C_2O_4)_3(lone pair)]\cdot 4H_2O$ (A = NH_4, K)	1.14		*n*
$[Mo(S_2CN(n\text{-}Bu)_2)_3(NO)]$	1.13	92	*o*
$[V(S_2CNEt_2)_3O]$	1.13	96	*p*
$[Nb(S_2CNEt_2)_3O]$	1.11	98	*p*
$[Sn(S_2CNEt_2)_3Me]$	1.06?		*q*
$[Te(S_2CNEt_2)_3Ph]$	1.05	91	*r*
$(Et_4N)[Pb(S_2COEt)_3(lone pair)]$	0.98		*s*
$[Sn(NO_3)_3Me]$			*t*

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Table IX. Fractional Contribution of the Unidentate to the Total Repulsion Coefficient *X*

b	A	B_1	B_2	C_1	C_2	C_3
			$n = 1$			
0.8	0.1757		0.1749			
0.9	0.1752		0.1745	0.1735		
1.0	0.1746		0.1739	0.1724		
1.1	0.1738	0.1730		0.1712		
1.2	0.1732	0.1720		0.1702		
1.3	0.1723	0.1716		0.1689		0.1719
1.4	0.1713					0.1737
1.5	0.1702					0.1697
			$n = 6$			
0.8	0.209		0.206	0.191		
0.9	0.208	0.199		0.185		
1.0	0.209	0.191		0.178		
1.1	0.207	0.187		0.172		
1.2	0.206	0.187		0.172		
1.3	0.204			0.181	0.211	
1.4	0.202	0.194			0.196	
1.5	0.200	0.196			0.170	
			$n = 12$			
0.8	0.228	0.210			0.189	
0.9	0.228	0.197		0.176		
1.0	0.227	0.185		0.166		
1.1	0.225	0.182		0.166		
1.2	0.225	0.185		0.172	0.243	
1.3	0.223	0.197		0.188	0.235	
1.4	0.219		0.210	0.185	0.216	
1.5	0.217		0.200		0.168	

Discussion

The relative energies of the various stereochemistries normalized to those for the capped octahedron A are shown in Table VII. The differences in energy between various minima are fairly small and probably not chemically significant, particularly in view of crystal packing energies and the chemical difference between the unidentate and the bidentate donor atoms.

Nevertheless the question arises as to what chemical factor, if any, favors particular stereochemistries. A possible clue to one such factor is given in Table VIII, which lists all known structures for compounds of stoichiometry $M(bidentate)_3(unidentate)$. From these limited data it can be seen that where the seventh coordination site is occupied by a lone pair of electrons or by unidentate ligands which can be formally considered to carry a negative charge and which can be envisaged as forming strong covalent metal–ligand bonds the complexes formed are of stereochemistry C_1. The fraction of the total repulsion coefficient *X* associated with the unidentate ligand is shown in Table IX; it is clear that a unidentate ligand in structure C_1 always experiences less repulsion than do unidentate ligands in any of the other structures. However the stabilization of this structure with the nitrosyl ligand should also be noted.

The larger repulsion associated with those unidentate ligands which form compounds of structure C_1 is also observed in the detailed structures of these compounds. Table VIII also lists the observed average angle between the metal–unidentate ligand bond and the neighboring metal–ligand bonds for stereochemistry A (that is, average of ϕ_B, ϕ_D, and ϕ_F), stereochemistry B_1 (average of ϕ_B, ϕ_C, ϕ_D, and ϕ_F), and stereochemistry C_1 (average of ϕ_B, ϕ_C, ϕ_F, and ϕ_G). The agreement between observed and predicted bond angles for stereochemistry A (75 and 76°, respectively, for $b = 1.2$) and stereochemistry B_1 (82 ± 3 and 82°, respectively) is very good, but for stereochemistry C_1 the observed average angle of 93 ± 4° (or 97° for the doubly charged O^{2-} unidentate), with all bidentate ligands lying on the same side of the metal atoms, is significantly greater than the predicted value of about 86° for the appropriate values of *b*.

This structural observation that charged ligands stabilize one of the possible isomers by preferentially occupying the less sterically hindered sites is also noted in five-coordinate complexes.[8]

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)$_3$.

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Notes

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Solvent-Assisted Racemization of Tris-Chelate Complexes

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Received February 13, 1974 AIC40100S

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.

Method

The repulsion energy coefficients were calculated as before,[2] with the additional variable R, the ratio between the metal-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 unidentate ligand,[3] namely, the twisting around a real or pseudo C_3 axis, operation A_6 of ref 1, or the "Bailar twist."

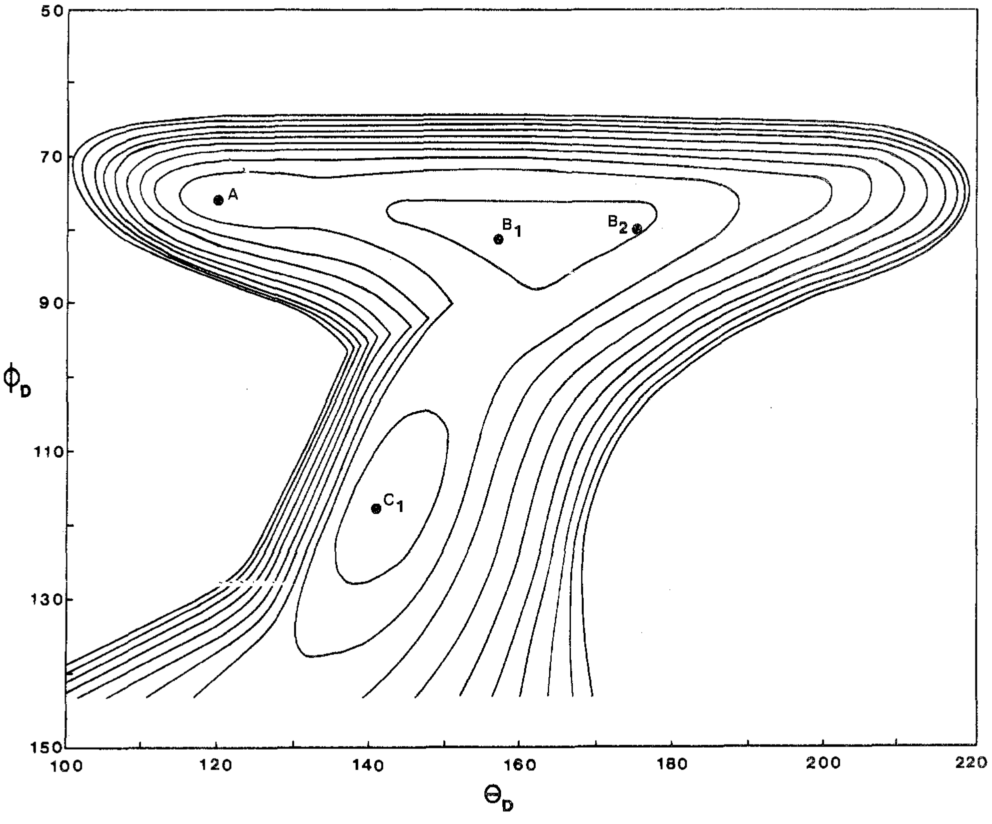

Figure 1. Potential energy surface for the racemization of M(bidentate)$_3$(unidentate); $R = 1.00$, $b = 1.2$, $n = 6$. The repulsion energies have been normalized so that successive contours are for 1% energy increases above the bottom of the potential energy surface at stereochemistry B_1.

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

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[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).