$FeCl_3$ is the cause of the distortion. In an attempt to confirm this, the infrared spectrum from 4000 to 600 cm^{-1} was observed *vs.* benzene as a reference. Only those bands which possess large intensities and are different from liquid benzene would be expected to appear in this spectrum. Two such bands were observed at 2932 ± 7 and 2864 ± 7 cm^{-1}. These are benzene C–H stretching modes which for unperturbed liquid benzene fall in the region 3062–3048 cm^{-1}.[12] Benzene π complexes often show C–H stretching modes different from liquid benzene. For example, $(C_6H_6)_2W$ shows maxima at 3012 and 2898 cm^{-1}.[12] We conclude that benzene is in fact π bonded to the iron causing a slight displacement of the chlorines away from the benzene, destroying the $FeCl_3$ plane.

Further comparisons are in order. $FeCl_3Br^-$ contains a pyramidal $FeCl_3$ group for which infrared maxima have been assigned.[13] The Fe–Cl bands compare favorably with those of $FeCl_3$ in benzene (see Table I). For completeness the spectral data reported for $FeCl_4^-$ both distorted and regular tetrahedral are also included in the table. Note that the strongest bands in these spectra fall between the two stretching maxima of $FeCl_3$ in benzene; apparently no measurable amount of $FeCl_4^-$ is present in our solutions.

No π-bonded benzene adduct appears to have been reported with more than two benzenes per molecule.[12] If two benzene molecules were coordinated to the iron, one would expect axial coordination and D_{3h} symmetry, by analogy to $FeCl_3$ behavior in water.[14] Two benzenes coordinated so as to destroy the Fe–Cl plane might be expected to give rise to nonequivalent chlorines and to a splitting in the doubly degenerate modes, $\nu_3(E)$ and $\nu_4(E)$. No splitting in $\nu_3(E)$ was detected. All of the evidence is consistent with an $FeCl_3 \cdot C_6H_6$ adduct in solution possessing C_{3v} symmetry.

Registry No. $FeCl_3$, 7705-08-0; $FeCl_3 \cdot C_6H_6$, 40200-01-9; benzene, 71-43-2.

(12) M. Tsutsui, M. N. Levy, A. Nakamura, M. Ichikawa, and K. Mori, "Introduction to Metal π-Complex Chemistry," Plenum Press, New York, N. Y., 1970, pp 61, 62.
(13) C. A. Clausen, III, and M. L. Good, *Inorg. Chem.*, 9, 220 (1970).
(14) A. L. Marston and S. F. Bush, *Appl. Spectrosc.*, 26, 579 (1972).

Stereochemistry of Five-Coordination.
I. Monodentate Ligands

D. L. Kepert

Five-coordinate molecules are of considerable interest as they are known with trigonal-bipyramidal (D_{3h} symmetry), square-pyramidal (C_{4v} symmetry), or intermediate (C_{2v} symmetry) stereochemistry. In addition to the comparable stability of these isomers, there is also the possibility of low activation energies leading to rapid intramolecular interconversion.

However there does not appear to have been a completely satisfactory explanation for this variability in stereochemistry or for the detailed stereochemistry of the square pyramidal and intermediate isomers.

Stereochemical calculations based on the minimization of ligand–ligand repulsion energies using an inverse relation between the potential energy and the distance between the donor atoms,[1] and also an inverse square relation,[2] have not been very successful. The predicted bond angles for the square pyramid were not in agreement with those experimentally observed, the calculated displacement of the central metal atom from the basal square plane of donor atoms being much greater than that observed.

These calculations are now extended in more detail for the following reasons: (a) to determine the relative stability of the different isomers, (b) to predict more precisely the geometry of the square pyramid and intermediate isomers, (c) to obtain a precise mapping of the potential energy surface because of the interest in the intramolecular rearrangement of five-coordinate molecules, (d) to examine if this approach to stereochemistry can be extended to cases where all bonds are not equivalent, and (e) to provide a basis enabling a comparison to be made with five-coordinate molecules containing bidentate[3] and polydentate[4] ligands.

Method

The stereochemical arrangement of a number of ligand donor atoms surrounding a central atom may be calculated by the minimization of the total ligand–ligand repulsion energy U obtained by summing over all donor atom–donor atom repulsions. It is assumed that the repulsive energy u_{ij} between any two donor atoms i and j is proportional to some inverse power n of the distance d_{ij} between them. If all bond lengths are equal, that is all donor atoms lie on the surface of a sphere of radius r, then the results can be expressed in the form

$$U = \sum_{ij} u_{ij} = \sum_{ij} ad_{ij} = aXr^{-n}$$

where a is the proportionality constant and X is the repulsive energy coefficient which can be calculated from the value of n and the geometry of the coordination polyhedron.

The most appropriate value of n cannot be known exactly but certainly lies between the limits of 1 (for a purely coulombic interaction) and 12. Fortunately conclusions based on calculations on eight-coordinate[5-7] and six-coordinate[8] complexes have not been very dependent upon the assumed value of n.

Figure 1 defines the general stereochemistry for five-coordination. The twofold axis passes through the central metal atom M and the donor atom E. The angles between this axis and the bonds to each of the pairs of donor atoms A,C and B,D are denoted by ϕ_A and ϕ_B, respectively. The trigonal bipyramid is defined by $\phi_A = 90.0°$ and $\phi_B = 120.0°$ (or $\phi_A = 120.0°$ and $\phi_B = 90.0°$), and the square pyramid is defined by $\phi_A = \phi_B$.

The distances between the donor atoms are given by

$AB = AD = BC = CD = (2 - 2 \cos \phi_A \cos \phi_B)^{1/2} r$

$AC = (2 \sin \phi_A)r$

$AE = CE = (2 - 2 \cos \phi_A)^{1/2} r$

$BD = (2 \sin \phi_B)r$

$BE = DE = (2 - 2 \cos \phi_B)^{1/2} r$

(1) J. Zemann, *Z. Anorg. Allg. Chem.*, **324**, 241 (1963).
(2) R. B. King, *J. Amer. Chem. Soc.*, **92**, 6455 (1970).
(3) D. L. Kepert, *Inorg. Chem.*, **12**, 1942 (1973).
(4) D. L. Kepert, work in progress.
(5) D. L. Kepert, *J. Chem. Soc.*, 4736 (1965).
(6) D. G. Blight and D. L. Kepert, *Theor. Chim. Acta*, **11**, 51 (1968).
(7) D. G. Blight and D. L. Kepert, *Inorg. Chem.*, **11**, 1556 (1972).
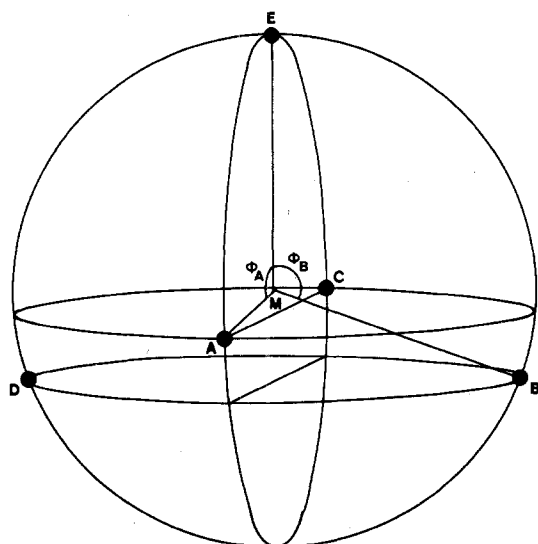(8) D. L. Kepert, *Inorg. Chem.*, **11**, 1561 (1972).

Figure 1. General stereochemistry for M(monodentate)$_5$.

When the bond length ME is equal to r', the other four bond lengths remaining equal to r, and when R is defined as the ratio r'/r, these expressions become

$$AB = AD = BC = CD = (2 - 2 \cos \phi_A \cos \phi_B)^{1/2} r$$

$$AC = (2 \sin \phi_A) r$$

$$AE = CE = (1 + R^2 - 2R \cos \phi_A)^{1/2} r$$

$$BD = (2 \sin \phi_B) r$$

$$BE = DE = (1 + R^2 - 2R \cos \phi_B)^{1/2} r$$

Alternatively when the bond lengths MB and MD are equal to r', the other three bond lengths remaining equal to r, and R is again defined as the ratio r'/r, these expressions become

$$AB = AD = BC = CD = (1 + R^2 - 2R \cos \phi_A \cos \phi_B)^{1/2} r$$

$$AC = (2 \sin \phi_A) r$$

$$AE = CE = (2 - 2 \cos \phi_A)^{1/2} r$$

$$BD = (2R \sin \phi_B) r$$

$$BE = DE = (1 + R^2 - 2R \cos \phi_B)^{1/2} r$$

Results and Discussion

Potential energy surfaces for five equivalent ligands are shown in Figures 2-4, for n having values of 1, 6, and 12, respectively. The repulsive energies have been normalized so that the minimum energy is exactly equal to unity. The diagrams are symmetrical about the diagonal $\phi_A = \phi_B$ due merely to an interchange of the A and B labels on the ligand atoms. The minima at $\phi_A = 90.0°$, $\phi_B = 120.0°$ and at $\phi_A = 120.0°$, $\phi_B = 90.0°$ correspond to the trigonal bipyramid, while the saddle between these minima at $\phi_A = \phi_B$ corresponds to the square pyramid. There is no potential energy barrier between these two stereochemistries along the "reaction coordinate" shown by the broken line.

Removal of the restrictions imposed by the C_2 axis showed that each of the above minima were true minima.

The values of the repulsive energy coefficients and the corresponding angular parameters for the two limiting stereochemistries are collected in Table I.

Contrary to previous calculations of stereochemistries based on minimization of the ligand–ligand repulsive energy, the calculated stereochemistry in the case of the square pyramid is very dependent upon the assumed value of n. The dependence of the "reaction coordinate" upon n is
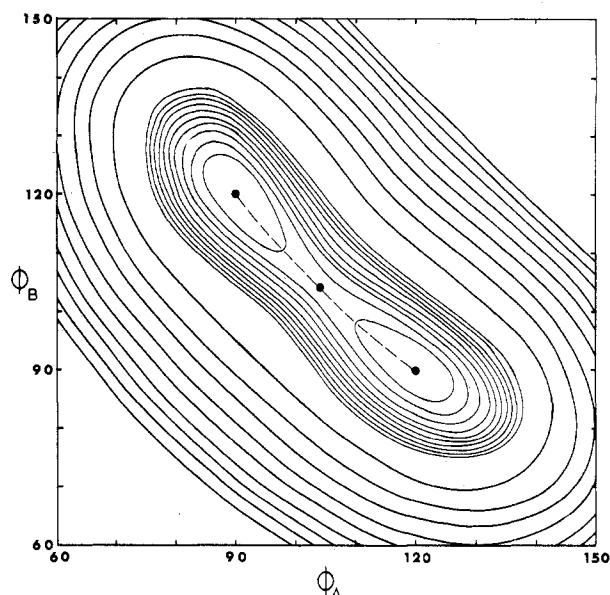

Figure 2. Potential energy surface for M(monodentate)$_5$ ($n = 1$). The faint contour lines are for 0.1% energy increases, and the dark contour lines for 1% energy increases, above the bottom of the potential energy surface corresponding to the trigonal bipyramid. The "reaction coordinate" is shown by the broken line.
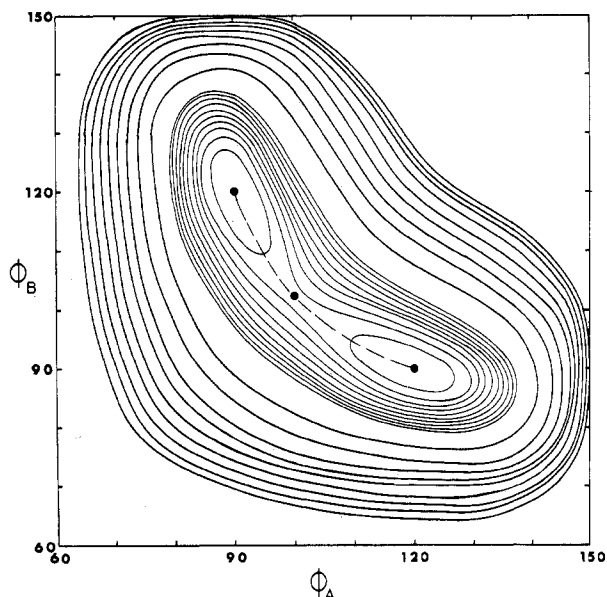

Figure 3. Potential energy surface for M(monodentate)$_5$ ($n = 6$). The faint contour lines are for 1% energy increases, and the dark contour lines for 10% energy increases, above the bottom of the potential energy surface corresponding to the trigonal bipyramid. The "reaction coordinate" is shown by the broken line.

Table I. Angular Parameters and Ligand–Ligand Repulsion Coefficients for Trigonal-Bipyramidal and Square-Pyramidal Stereochemistries

	$n = 1$	$n = 6$	$n = 12$
	Trigonal Bipyramid		
ϕ_A, deg	90.0	90.0	90.0
ϕ_B, deg	120.0	120.0	120.0
X	6.4747	0.8767	0.0981
	Square Pyramid		
ϕ_A, deg	104.1	101.3	98.9
ϕ_B, deg	104.1	101.3	98.9
X	6.4837	0.8898	0.0992

shown in Figure 5. It can be seen that as the value of n increases, that is as the ligand atoms become less compressible,
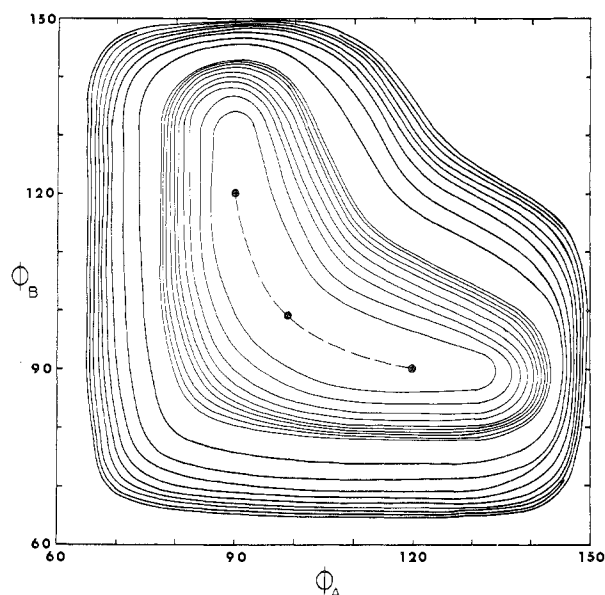
Figure 4. Potential energy surface for M(monodentate)$_5$ ($n = 12$). The faint contour lines are for 10% energy increases, and the dark contour lines for 100% energy increases, above the bottom of the potential energy surface corresponding to the trigonal bipyramid. The "reaction coordinate" is shown by the broken line.
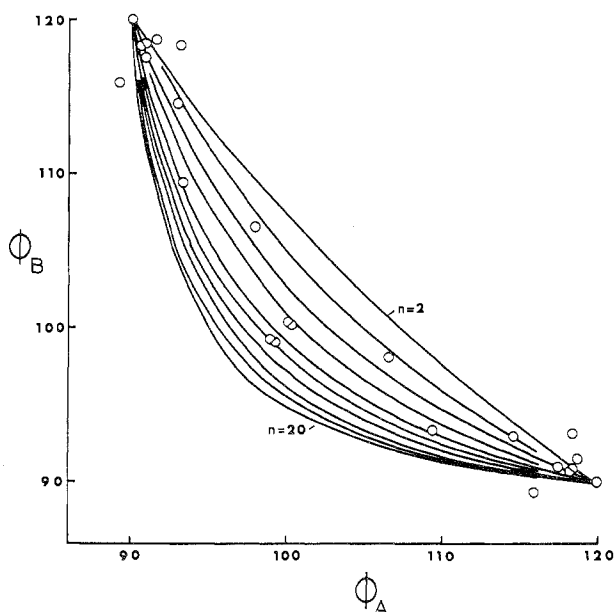

Figure 5. Dependence of "reaction coordinate" upon n. $n = 2$ (top curve), 4, 6, 8, 10, 12, 14, 16, 18, and 20 (bottom curve).

the stereochemistry becomes more nearly that of a "half-octahedron" with the length of all polyhedral sides equal and with the metal atom more near the center of the square plane of donor atoms.

Those molecules containing five equivalent ligands which have been completely structurally characterized are listed in Table II and are also marked in Figure 5. Allowing for the flatness of the potential energy surfaces in the region near the trigonal bipyramid, it can be seen that the most appropriate value of n lies between 6 and 10. These results clearly show that whereas it is not possible to predict that any molecule will have an undistorted trigonal-bipyramidal or square-pyramidal stereochemistry, it is possible to predict that any distortion can only be along a well-defined direction. For example although the two independent [Ni(CN)$_5$]$^{3-}$ anions in the tris(ethylenediamine)chromium(III) salt have widely

Table II. Structural Parameters for Five-Coordinate Molecules

	ϕ_A, deg	ϕ_B, deg	Ref
[Cr(NH$_3$)$_6$][Cu^{II}Cl$_5$]	90.0	120.0	a
[Cr(NH$_3$)$_6$][Cu^{II}Br$_5$]	90.0	120.0	b
PPh$_5$	91.5	118.7	c
[Ni(o-phen)$_3$][Mn(CO)$_5$]	90.6	118.2	d
	90.9	117.5	
[Ni^{II}(C$_6$H$_9$O$_5$P)$_5$](ClO$_4$)$_2$	90.8	118.4	e
(Ph$_4$As)$_2$[Fe^{III}(N$_3$)$_5$]	93.1	118.3	f
[Co^{II}(CNMe)$_5$](ClO$_4$)$_2$	89.2	115.9	g
[Co^{II}(2-MeC$_5$H$_4$NO)$_5$](ClO$_4$)$_2$	93.0	114.5	h
SbPh$_5$	98.0	106.5	i
[Cr(en)$_3$][Ni^{II}(CN)$_5$]·1.5H$_2$O	93.3	109.4	j
	100.1	100.3	
[Cr(pn)$_3$][Ni^{II}(CN)$_5$]·2H$_2$O	99.0	99.2	k

a K. N. Raymond, D. W. Meek, and J. A. Ibers, *Inorg. Chem.*, 7, 1111 (1968). b S. A. Goldfield and K. N. Raymond, *ibid.*, 10, 2604 (1971). c P. J. Wheatley, *J. Chem. Soc.*, 2206 (1964). d B. A. Frenz and J. A. Ibers, *Inorg. Chem.*, 11, 1109 (1972). e E. F. Riedel and R. A. Jacobson, *Inorg. Chim. Acta*, 4, 407 (1970). f J. Drummond and J. S. Wood, *Chem. Commun.*, 1373 (1969). g F. A. Cotton, T. G. Dunne, and J. S. Wood, *Inorg. Chem.*, 4, 318 (1965). h B. A. Coyle and J. A. Ibers, *ibid.*, 9, 767 (1970). i P. J. Wheatley, *J. Chem. Soc.*, 3718 (1964). j K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *Inorg. Chem.*, 7, 1362 (1968). k A. Terzis, K. N. Raymond, and T. G. Spiro, *ibid.*, 9, 2415 (1970).
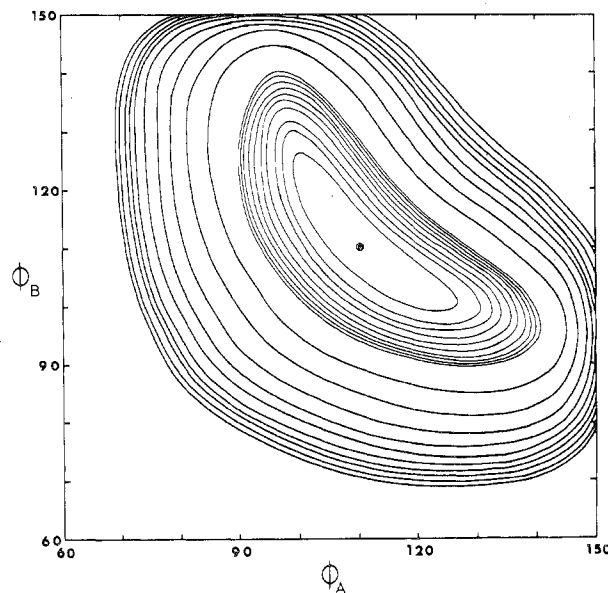

Figure 6. Potential energy surface for M(monodentate')(monodentate)$_4$ ($n = 6$). Bond length ratio $R = 0.5$. The faint contour lines are for 1% energy increases, and the dark contour lines for 10% energy increases, above the bottom of the potential energy surface.

different structures, they have virtually identical values for the ligand–ligand repulsion energy.

Extension of these calculations shows that the relative stability of the square pyramid and the trigonal bipyramid is changed if all ligands are not assumed to be equal.

For compounds of stoichiometry M(monodentate')(monodentate)$_4$, typical potential energy surfaces for $n = 6$ are shown in Figures 6 and 7. For a bond length ratio R of 0.5, a single minimum occurs on the potential energy surface at $\phi_A = \phi_B$ (Figure 6), clearly predicting that the square pyramid will be the most stable stereochemistry. Examples of compounds with this structure are (NH$_4$)$_2$[V^{IV}O(NCS)$_4$]·5H$_2$O[9] and [Co^{II}(ClO$_4$)(Ph$_2$MeAsO)$_4$](ClO$_4$).[10] As the bond length

(9) A. C. Hazell, *J. Chem. Soc.*, 5745 (1963).
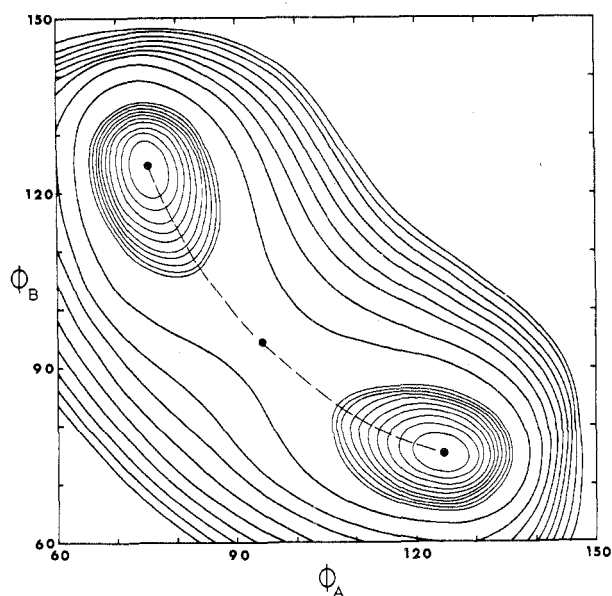(10) P. Pauling, G. B. Robertson, and G. A. Rodley, *Nature (London)*, 207, 73 (1965).

Figure 7. Potential energy surface for M(monodentate')(mono-dentate)$_4$ ($n = 6$). Bond length ratio $R = 1.5$. The faint contour lines are for 1% energy increases, and the dark contour lines for 10% energy increases, above the bottom of the potential energy surface.

Figure 8. Potential energy surface for M(monodentate')$_2$(mono-dentate)$_3$ ($n = 6$). Bond length ratio $R = 1.5$. The faint contour lines are for 1% energy increases, and the dark contour lines for 10% energy increases, above the bottom of the potential energy surface.

ratio increases to unity, this minimum becomes shallower and then symmetrically splits into two minima corresponding to the two equivalent trigonal bipyramids shown earlier (Figure 3). For bond length ratios greater than unity, these two minima progressively deepen and move further apart (Figure 7) as the bond angles approach the tetrahedral values ($\phi_A = 54.7$, $\phi_B = 125.3°$). An example of this structure is [Co(AuPPh$_3$)(CO)$_4$].[11]

Precise predictions regarding the detailed stereochemistry cannot be made because the results are again dependent upon the assumed value of n and because it cannot even be assumed that the same value of n will be applicable for the different kinds of interactions between the different donor atoms.

For compounds of stoichiometry M(monodentate')$_2$-(monodentate)$_3$, typical potential energy surfaces for $n = 6$ are shown in Figures 8 and 9. For two long bonds and three short bonds, as the bond length ratio R is progressively increased above unity the potential energy minimum at $\phi_A = 120.0$, $\phi_B = 90.0°$ (Figure 3) progressively deepens (Figure 8). This corresponds to the increasing stability of the trigonal bipyramid with the longer bonds occupying the two axial sites and the shorter bonds occupying the three equatorial sites and ultimately leads to the planar-triangular structure.

Alternatively as R is progressively decreased from unity, it is the other potential minimum at $\phi_A < \phi_B$ which deepens and moreover progressively moves to lower values of ϕ_A and ϕ_B (Figure 9). This corresponds to the two shorter bonds occupying the less crowded equatorial sites, even though this places these shorter bonds closer together. Again the precise angular parameters are found to be dependent upon the value of n. It is not until R becomes very low ($R \leqslant 0.7$ for $n = 1$, $R \leqslant 0.4$ for $n = 6$, $R \leqslant 0.3$ for $n = 12$) that the interactions between these short bonds dominate and the trigonal bipyramid at $\phi_A = 120.0$, $\phi_B = 90.0°$ becomes the most stable stereochemistry again and ultimately approaches a simple two-coordinate linear structure.

(11) B. T. Kilbourn, T. L. Blundell, and H. M. Powell, *Chem. Commun.*, 444 (1965).
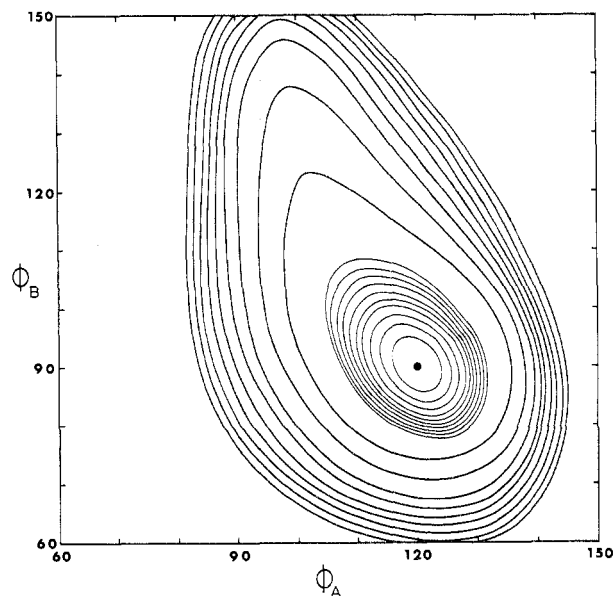

Figure 9. Potential energy surface for M(monodentate')$_2$(mono-dentate)$_3$ ($n = 6$). Bond length ratio $R = 0.75$. The faint contour lines are for 1% energy increases, and the dark contour lines for 10% energy increases, above the bottom of the potential energy surface.
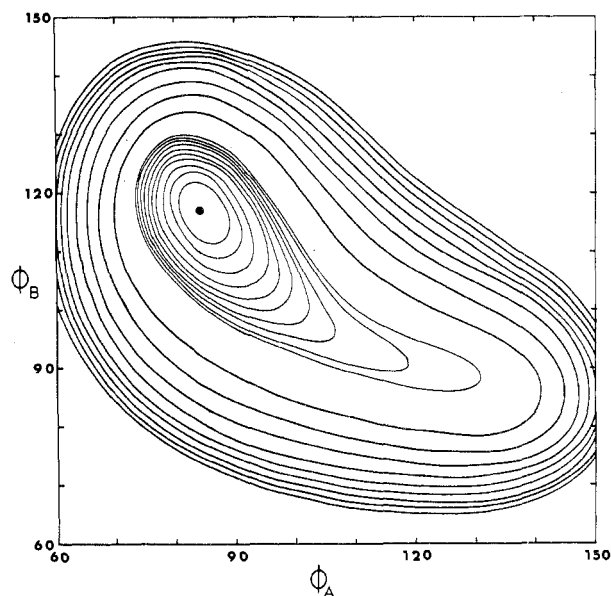
In no case for M(monodentate')$_2$(monodentate)$_3$ does the square pyramid become a minimum on the potential energy surface. The difference in energy between the square pyramid and the most stable trigonal bipyramid progressively increases as the bond length ratio progressively departs from unity.

It is therefore not unexpected that only the trigonal bipyramids at $\phi_A = 120.0$, $\phi_B = 90.0°$ (with the two equivalent ligands occupying the axial sites) and at $\phi_A < \phi_B$ (with the two equivalent ligands occupying two of the equatorial sites) are known. The first is known for BiCl$_2$Ph$_3$[12] and a series of trimethylamine complexes [AlH$_3$(Me$_3$N)$_2$],[13]

(12) D. M. Hawley, G. Ferguson, and G. S. Harris, *Chem. Commun.*, 111 (1966).
(13) C. W. Heitsch, C. E. Nordman, and R. W. Parry, *Inorg. Chem.*, 2, 508 (1963).

$[TiBr_3(Me_3N)_2]$,[14] $[VCl_3(Me_3N)_2]$,[15] and $[CrCl_3(Me_3N)_2]$.[16] The second type is found in $[Cu(PhOCH_2COO)_2(H_2O)_3]$,[17] the dimethylimidazole derivative $[CuCl_2(C_5H_8N_2)_3]$,[18] $[RuCl_2(Ph_3P)_3]$,[19] $[CoBr_2(Ph_2PH)_3]$, and $[NiI_2(Ph_2PH)_3]$,[20] four tertiary phosphine derivatives of the type $[Ni(CN)_2-(phosphine)_3]$,[21] and the anion of $[SnMe_2Cl(terpy)]-[SnMe_2Cl_3]$.[22] The angular parameters corresponding to the individual stereochemistries lie in the trough between the trigonal bipyramid at $\phi_A < \phi_B$ and the saddle at $\phi_A = \phi_B$ corresponding to the square pyramid in a similar manner to that observed for complexes with five equivalent ligands. Again a more detailed comparison is not justified.

The stereochemistry of the d^8 complex $[PdBr_2(C_{14}H_{13}-P)_3]$[23] is best considered as a square plane with one additional long bond normal to the plane and, like d^8 square-planar complexes themselves, cannot be rationalized on the basis of ligand–ligand repulsion energies.

Energy factors for five-coordination other than ligand–ligand repulsion energies have been discussed in detail elsewhere.[24]

(14) B. J. Russ and J. S. Wood, *Chem. Commun.*, 745 (1966).
(15) P. T. Greene and P. L. Orioli, *J. Chem. Soc. A*, 1621 (1969).
(16) G. W. A. Fowles, P. T. Greene, and J. S. Wood, *Chem. Commun.*, 971 (1967).
(17) C. V. Goebel and R. J. Doedens, *Inorg. Chem.*, 10, 2607 (1971).
(18) F. Huq and A. C. Skapski, *J. Chem. Soc. A*, 1927 (1971).
(19) S. J. La Placa and J. A. Ibers, *Inorg. Chem.*, 4, 778 (1965).
(20) J. A. Bertrand and M. A. Plymale, *Inorg. Chem.*, 5, 879 (1966).
(21) D. W. Allen, F. G. Mann, I. T. Millar, H. M. Powell, and D. Watkin, *Chem. Commun.*, 1004 (1969); J. K. Stalik and J. A. Ibers, *Inorg. Chem.*, 8, 1084, 1090 (1969).
(22) F. W. B. Einstein and B. R. Penfold, *J. Chem. Soc. A*, 3019 (1968).
(23) J. W. Collier, F. G. Mann, D. G. Watson, and H. R. Watson, *J. Chem. Soc.*, 1803 (1964).
(24) For example, see C. Furlani, *Coord. Chem. Rev.*, 3, 141 (1968); P. L. Orioli, *ibid.*, 6, 285 (1971).
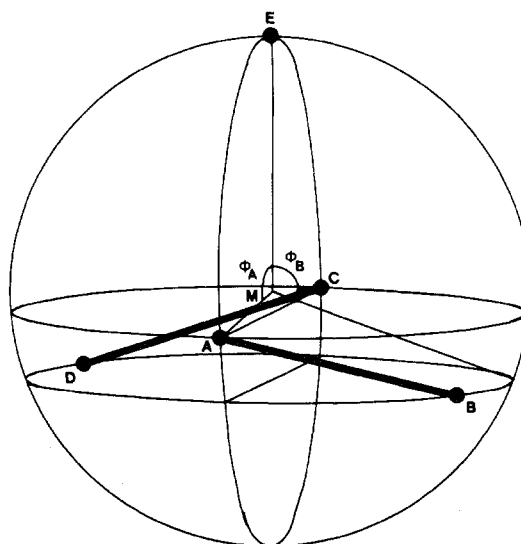

Stereochemistry of Five-Coordination. II. Compounds of Stoichiometry M(bidentate)$_2$(monodentate)

D. L. Kepert

Minimization of the total ligand–ligand repulsion energies has shown that the introduction of bidentate ligands into six-[1] and eight-coordinate[2] compounds significantly affects the relative stability of the different isomeric forms and also the activation energy for intramolecular isomerization. At least for the cases when all ligands are equivalent, the detailed stereochemistry can also be successfully predicted.

(1) D. L. Kepert, *Inorg. Chem.*, 11, 1561 (1972); 12, 1944 (1973).
(2) D. G. Blight and D. L. Kepert, *Inorg. Chem.*, 11, 1556 (1972).

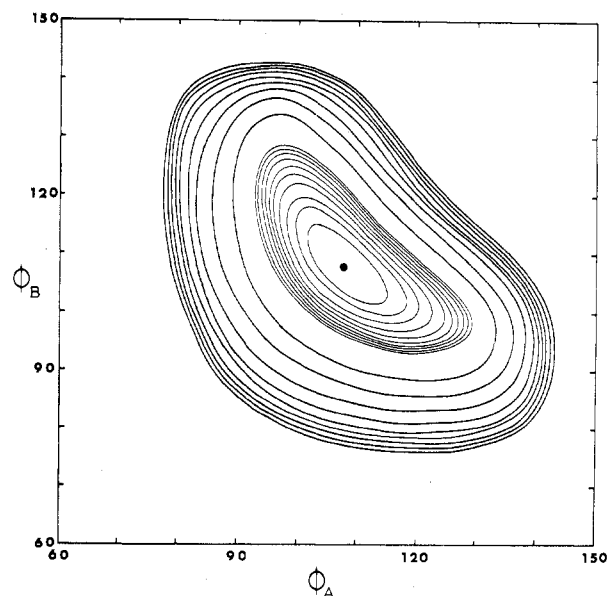**Figure 1.** General stereochemistry for M(bidentate)$_2$(monodentate).

Figure 2. Potential energy surface for M(bidentate)$_2$(monodentate) ($n = 6$). Normalized ligand bite, $b = 1.1$. The faint contour lines are for 1% energy increases, and the dark contour lines for 10% energy increases, above the bottom of the potential energy surface.

At present this simple model is the only way such predictions can be successfully made.

The effect of the introduction of two bidentate ligands into the five-coordinate structures[3] is examined in this paper.

Method

Figure 1 defines the general stereochemistry for M(bidentate)$_2$(monodentate), the bidentate ligands spanning the AB and CD edges. The angles between the twofold axis incorporating the metal–monodentate ligand bond and the two ends of each bidentate are denoted by ϕ_A and ϕ_B, respectively.

The regular trigonal-bipyramidal and regular square-pyramidal stereochemistries observed as the limiting cases in M(monodentate)$_5$ are necessarily distorted by the introduction of the bidentate ligands. The analogous stereochemistries for M(bidentate)$_2$(monodentate) will, for the sake of

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