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Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

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To cite this Article Holmes, Robert R.(1995) 'INFLUENCE OF d-ORBITAL OCCUPANCY ON THE GEOMETRY OF PENTACOORDINATED MOLECULES', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 98: 1, 387 — 398

To link to this Article: DOI: 10.1080/10426509508036963

URL: <http://dx.doi.org/10.1080/10426509508036963>

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INFLUENCE OF d-ORBITAL OCCUPANCY ON THE GEOMETRY OF PENTACOORDINATED MOLECULES¹

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(Received July 13, 1983)

A quantitative assessment of solid-state structural data on five coordinated compounds of both transition and main group elements establishes the geometrical change in the square pyramid as a function of d-orbital configuration. In terms of the trans basal angle θ , a variation in the range 140–174° is obtained. These angle variations are interpreted in terms of nonbonded repulsions between d-orbital electron density and bond electron density. Structural distortion from the trigonal-bipyramidal and square-pyramidal geometries are determined for the five-coordinated compounds by using a dihedral angle method. It is found that the local distortion coordinate for transition-metal complexes approximates the Berry intramolecular exchange coordinate. Main group pentacoordinated compounds follow this coordinate more closely.

It is known² that the square-pyramidal geometry assumed by some pentacoordinated phosphorus compounds has the phosphorus atom located out of the basal plane such that the trans basal angles, θ_{15} and θ_{24} , average 152°. This value was predicted by Zemann³ on the basis of a point-charge model. X-ray investigations on a variety of five-coordinated phosphorus compounds further show that the structural form assumed varies from near the idealized trigonal bipyramid (TBP) to the square pyramid (SP).^{2,4} These structures lie along a C_{2v} coordinate connecting the two limiting geometries and are supportive of the Berry pseudorotation mechanism⁵ frequently invoked⁶ to interpret dynamic NMR data indicative of intramolecular ligand exchange.

Although a great deal of structural work has been reported for five-coordinated transition-metal compounds, no quantitative assessment of the "preferred" geometry of the square-pyramidal form is available. The literature contains isolated references of possible variations. For example, high- and low-spin square-pyramidal Co(II) and Ni(II) complexes have been classified by Orioli⁷ in terms of metal atom displacement from the basal plane.

It is of interest to learn to what extent the geometry of the square pyramid changes across a transition series as the d configuration varies from d^0 to d^{10} . This paper treats this main feature of pentacoordinated compounds for both transition metals and main group derivatives. A rationale is offered for the observations in terms of variations in bonding attributed to changes in d-orbital configuration.

STRUCTURAL DISTORTION

Calculations

Sufficient structural data on five-coordinated complexes, largely from X-ray diffraction studies,⁸ are available for many of the transition elements to provide a

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basis for the treatment here. Similar to that formed with pentacoordinated phosphorus compounds, the transition-metal derivatives have structures that usually are intermediate in geometry between the trigonal bipyramid and the square pyramid. Adopting the procedure we used with phosphorus compounds,^{2,4,9} transition-metal structures may be interpreted in two ways. In one method,⁴ dihedral angles are calculated from the triangular faces of the polyhedron established by the positions of the five ligands attached to the metal. If these values are compared with the related values of the dihedral angles for the idealized trigonal bipyramid and square pyramid and their differences obtained, a measure of the structural distortion between these two forms may be established. The sum of the respective dihedral angle changes between the two idealized geometries $\sum_i |\delta_i(\text{TBP}) - \delta_i(\text{SP})|$ provides a common scale to compare structures of various five-coordinated compounds. The value of this sum is 217.9° when the trans basal angle θ for the reference square pyramid is 150°. Whenever the reference square pyramid has a different trans basal angle, it is necessary to recalculate this sum. These are given in Table I for square pyramids which have θ values that range from 140° to 174°.

A less elaborate procedure⁴ is to make use of the values of the axial and equatorial angles, θ_{15} and θ_{24} , respectively, relative to the dihedral angle δ_{24} as a measure of the distortion coordinate, a method first applied to acyclic five-coordinated transition metals by Muetterties and Guggenberger.¹⁰ The dihedral angle δ_{24} is the angle formed between normals to the trigonal-bipyramidal faces 124 and 245 that have the common equatorial edge 24 and is the one most intimately associated with the Berry exchange coordinate (Figure 1). This dihedral angle has a value of 53.1° for an idealized trigonal bipyramid but becomes 0° as edge 24 disappears on forming the square pyramid. Application of these methods to phosphorane compounds^{2,9} has shown close adherence to the Berry ligand exchange coordinate

TABLE I
Dihedral Angle Differences for Square-Pyramidal θ Values

θ , deg	$S = \sum_i \delta_i(\text{TBP}) - \delta_i(\text{SP}) $, deg
140	209.2
145	213.4
150	217.7
160	226.5
170	235.6
174	239.3

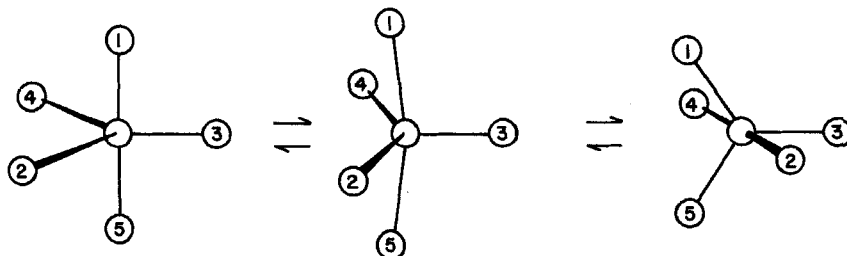


FIGURE 1 Berry intramolecular ligand exchange process.

in their structural distortions between the two reference five-coordinated geometries. A θ value of 152° is obtained for the limiting square pyramid.

PREFERRED SQUARE-PYRAMIDAL GEOMETRIES

By construction of graphs of θ_{15} and θ_{24} vs. δ_{24} for five-coordinated compounds of other elements in a given oxidation state, preferred square-pyramidal geometries may be established which should reveal interesting variations with changes in d-orbital configurations. To accomplish this, crystal structure data were analyzed¹¹ by making use of the bond angles between the ligands directly connected to the central atom.

Figures 2 and 3 show θ vs. δ_{24} plots for high- and low-spin Ni(II) compounds, respectively. A similar graph is given in Figure 4 for Si(IV) five-coordinated compounds. From these graphs, the θ value for δ_{24} equal to zero is determined. As with cyclic phosphoranes, the best θ value for a square-pyramid pentacoordinated silicon(IV) compound is 152° . For Ni(II) there is a considerable difference in the ideal θ value to use for a low-spin square-pyramidal nickel complex ($\theta = 173^\circ$) compared to a high-spin nickel complex ($\theta = 161^\circ$). Although high-spin Ni(II)

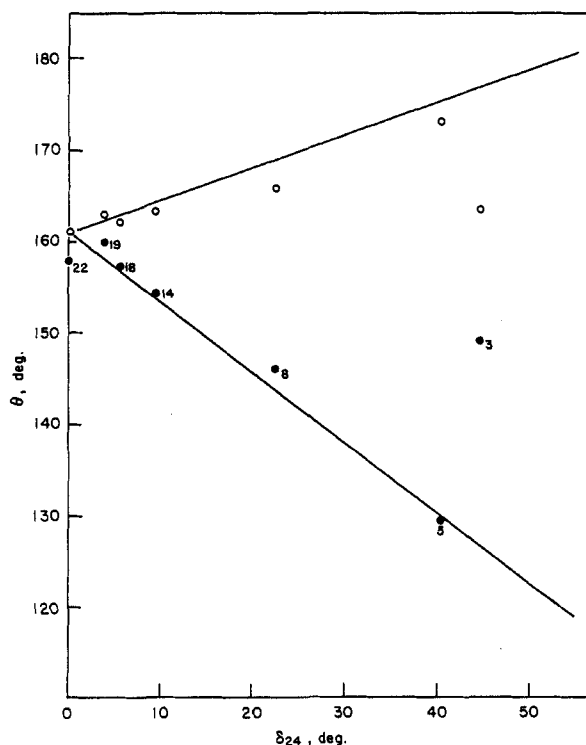


FIGURE 2 Variation of the axial angle, θ_{15} (open circles), and equatorial angle, θ_{24} (filled circles), vs. the dihedral angle, δ_{24} , as structural distortion for pentacoordinated high-spin nickel(II) compounds proceeds along a Berry type coordinate from a square pyramid toward a trigonal bipyramid. The numbers refer to specific compounds given in ref 8.

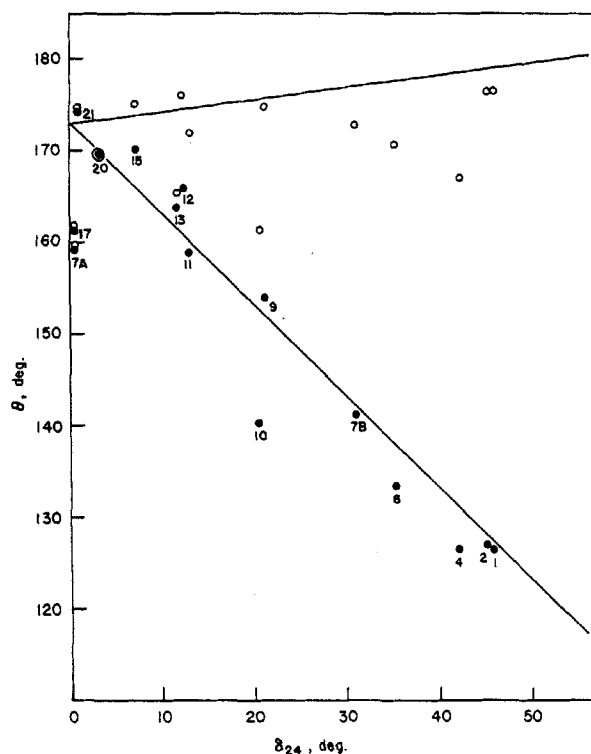


FIGURE 3 Variation of the axial angle, θ_{15} (open circles), and equatorial angle, θ_{24} (filled circles), vs. the dihedral angle, δ_{24} , as structural distortion for pentacoordinated low-spin nickel(II) compounds proceeds along a Berry type coordinate from a square pyramid toward a trigonal bipyramid. The numbers refer to specific compounds given in ref 8.

compounds available here are more sparse than their low-spin counterparts, the members span the range between the trigonal bipyramid and square pyramid in each case with the low-spin members perhaps displaying a more even distribution. The high-spin members show a slight preference for the square pyramid. A concentration toward the square pyramid is favored for high-spin d^8 five-coordinated complexes on the basis of the angular overlap model.¹²

Dihedral angle plots for five-coordinated compounds of Si(IV) and Cu(II) are given in Figures 5 and 6, respectively. These plots show close adherence of the Berry pseudorotational coordinate⁵ even more so than the θ plots.

Treating crystallographic data in a similar fashion for other five-coordinated elements results in the determination of preferred square pyramids from the basis set used. The θ values determined in this way are included in graphical form in Figure 7 as a function of d-orbital configuration. In Table II, each point shown in Figure 7 is identified in terms of the responsible pentacoordinated elements and their oxidation states.

As the d-orbital occupancy increases (starting at d^0 with $\theta = 152^\circ$) for the various five-coordinated transition elements, the limiting square pyramid at first becomes more pyramidal. At d^2 , θ is near 140° where a reversal in θ takes place. From d^2

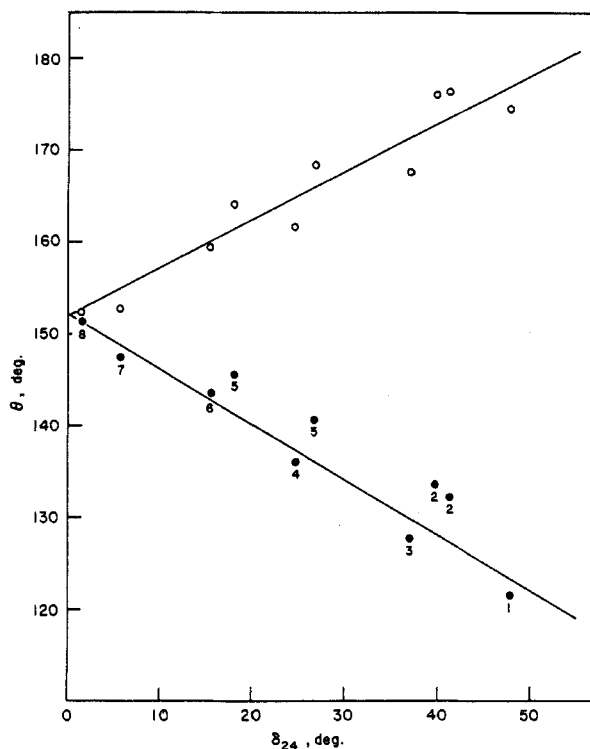


FIGURE 4 Variation of the axial angle, θ_{15} (open circles), and equatorial angle, θ_{24} , (filled circles), vs. the dihedral angle, δ_{24} , as structural distortion for pentacoordinated silicon(IV) compounds proceeds along the Berry coordinate from a square pyramid toward a trigonal bipyramid. The numbers refer to specific compounds given in ref 8.

to d^9 there is a gradual flattening of the square pyramid as θ rises from 140° , passing near 150° for high-spin d^5 Fe(III), and up to 174° for d^9 Cu(II). When d^{10} is reached, an abrupt decrease in θ to 152° is apparent as the limiting square pyramid returns to the starting configuration. Although the average values of θ for the cobalt(II) and nickel(II) structures follow this trend, the low-spin derivatives show a much higher θ value than that for the high-spin complexes, as already mentioned.

DISCUSSION

Repulsion Model

The variation in the trans basal angle as a function of d-orbital configuration, displayed in Figure 7, may be interpreted simply from the relative order of d-orbital energy levels of the square pyramid. For this purpose, it is instructive to refer to the energy correlation diagram along the pseudorotational coordinate connecting the trigonal bipyramid and square pyramid. Figure 8 portrays this coordinate¹³ and includes the symmetry changes encountered. In contrast to the D_{3h} trigonal bipyramid where d-orbital occupancy will exert a primary influence on relative bond lengths, the additional angular parameter present in the C_{4v} square pyramid allows

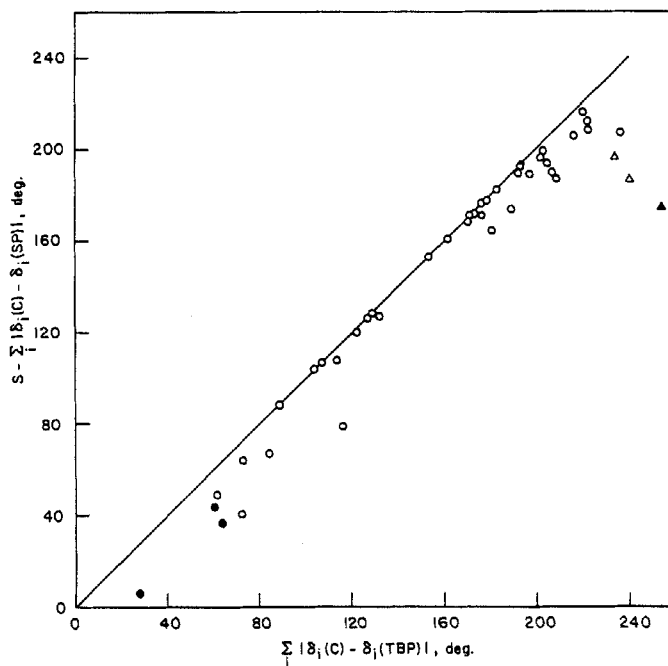


FIGURE 5 Sum of dihedral angles for pentacoordinated copper(II) compounds from a square-pyramid geometry vs. the sum from a trigonal bipyramid on a common reference scale. Compounds containing tripodal ligands (filled circles), constrained ligand systems (open triangles), or have hydrogen bonding present (filled triangle) are considerably displaced from the Berry coordinate.

d-orbital effects to be reflected in both bond distance and bond angle variations. It is reasonable that bond angle changes should preferentially occur in the absence of other controlling factors since less energy normally is required for bond bending compared to bond stretching.

In the model that follows, the interpretation of θ changes for square pyramids is given in terms of repulsions between nonbonding electrons in occupied d orbitals, largely antibonding with respect to the ligands in the MO scheme, and bond electron density.

The repulsion effects are seen more readily if the d orbitals are viewed in the square-pyramidal reference frame (Figure 9). Considering the low-spin case first, in the absence of π bonding and starting at d^0 with $\theta \cong 152^\circ$, the addition of nonbonding electrons to the lowest energy d_{xy} orbital causes a repulsion with the basal bond electron pairs which could be relieved by further lengthening of the basal bonds or preferentially by a decrease in θ since this electron density resides above the basal plane. In contrast, the occupancy of the e level, even with a uniform electron distribution in either the antibonding d_{xz} or d_{yz} orbital, would cause a repulsion with the basal bond electron density resulting in an expansion of θ . A similar unbalanced repulsion effect occurs at the a_1 level as the z^2 level is occupied, giving rise to an additional increase in θ toward 180° . Filling the $d_{x^2-y^2}$ orbital corresponding to the b_1 level, like the d_{xy} level, produces a repulsion which now decreases θ . Completion of the d shell at d^{10} once again gives a uniform d electron

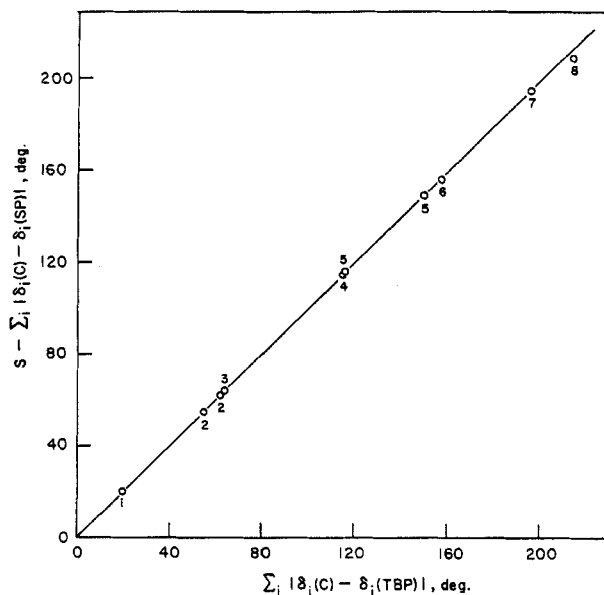


FIGURE 6 Sum of dihedral angles for pentacoordinated silicon(IV) compounds from a square-pyramidal geometry vs. the sum from a trigonal bipyramid on a common reference scale. The numbers refer to specific compounds given in ref 8.

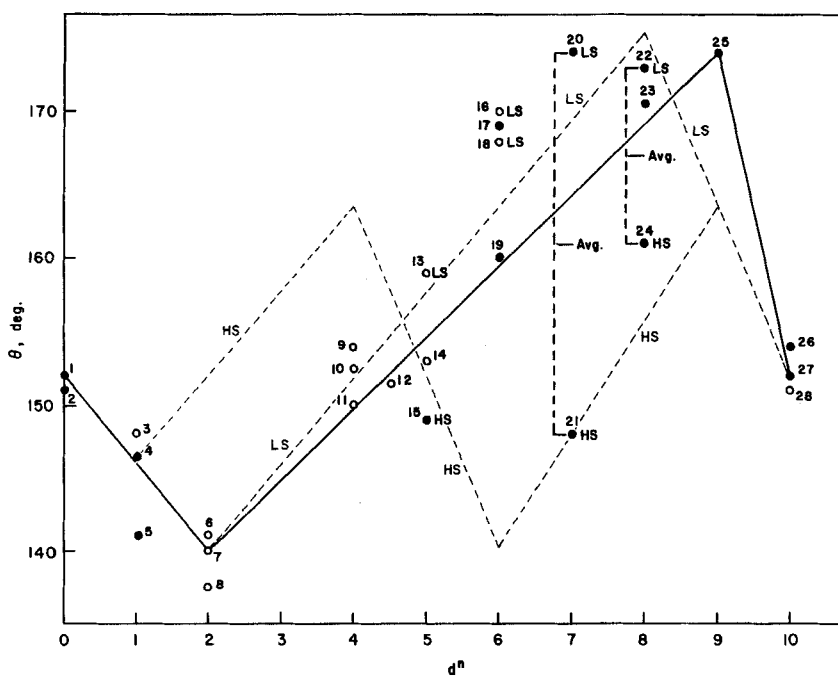


FIGURE 7 Variation of the trans basal angle θ for preferred square pyramids vs. the d-orbital configuration (d^n) of the central element for pentacoordinated compounds. The points are identified in Table II. Filled circles refer to points determined with four or more compounds. Open circles refer to points based on three or less compounds. LS = low spin. HS = high spin. The solid line represents the general trend of θ vs. d^n . The light dashed line is a superposition of Figure 10 representing a model description which differentiates between high-spin and low-spin systems.

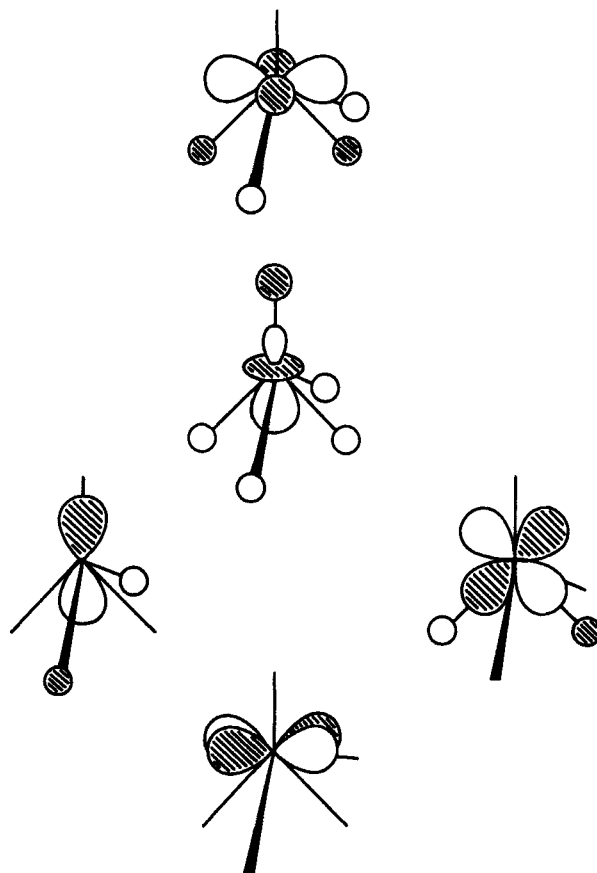


FIGURE 9 Antibonding d orbitals ascending in increasing energy in a square-pyramidal geometry. Although the relative energies will modify somewhat as θ changes, there are no crossovers for the θ range, $140\text{--}174^\circ$, based on an extended-Hückel treatment.¹³

These changes in the square-pyramidal geometry expected from this model are summarized graphically in Figure 10. It reproduces the main structural changes experimentally encountered (Figure 7) other than the drop in θ expected on going from low-spin d^8 to the d^9 configuration. The model graph in Figure 10 is constructed by using the θ range observed for square-pyramidal compounds, i.e., $140\text{--}175^\circ$. With θ for d^0 , d^{10} , and high-spin d^5 at 152° , θ for d^9 is established as $\sim 163^\circ$. This value is also used for the peak in θ for high-spin d^4 . Superposition of Figure 10 on Figure 7 by way of dashed lines shows the degree of agreement with the experimental data.

With this model, the much higher values for θ for low-spin Co(II) and Ni(II) complexes compared to their high-spin counterparts is easily rationalized. Transfer of a nonbonding d electron from the $d_{x^2-y^2}$ orbital to either the e level for Co(II) or the a_1 level for Ni(II), on going from high to low spin, transfers electron density from the region above (toward the apical ligand) the metal-basal ligand bonds to the region below these bonds. Consequently, an increase in θ is expected, consistent

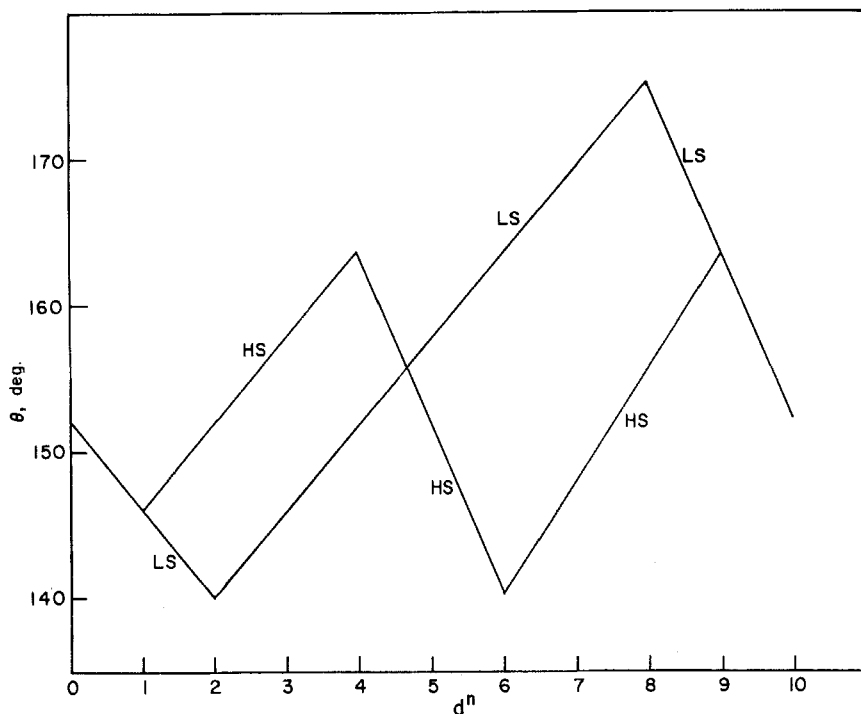


FIGURE 10 Repulsion model description of the variation of the trans basal angle θ of the square pyramid vs. d-orbital configuration (d^n) of the central element of pentacoordinated compounds. HS = high spin. LS = low spin.

with the sizeable change observed in each case. Other low-spin complexes are displaced equally to the high θ side of the average trend given in Figure 7, e.g., low-spin d^6 Co(III).

If π bonding effects are considered, we should expect some modification from the model just presented. Following Rossi and Hoffmann,¹³ some reduction of the nonbonding d electron density is expected to account for the mixing of antibonding d character into basal bonds (via e and b_1 orbitals) or into the apical bond (via the a_1 orbital) in σ -bond formation and, in the case of π bonding, mixing d character into basal bonds from the xz , yz , z^2 , and xy orbitals and xz and yz character into the apical bond. It is noted that all of the d^1 and d^2 square-pyramidal complexes used to construct Figure 9 have apical π -donor ligands which should add electron density to the xz and yz orbitals that are then hybridized toward the apical ligand. Repulsion of this electron density and the basal electron pairs should help to lower θ .

Many low-spin d^7 and d^8 square-pyramidal complexes have strong basal π -acceptor ligands and only weakly σ -bonding apical ligands.⁷ This should reduce electron density preferentially in the d_{xy} orbital in forming the π -bond system and increase electron pair bond repulsion among the strongly covalent basal bonds, both effects tending to increase θ . At d^9 , the expected drop in θ value is not experimentally observed (Figure 7). Perhaps, because the $d_{x^2-y^2}$ orbital is the

highest energy orbital and is involved most strongly in metal-basal ligand anti-bonding, the repulsion effect is not as effective as the others.

Bond Parameters

Concerning the latter point, it is instructive to examine bond distance values for pentacoordinated derivatives that have identical ligands bonded to the different positions of either the trigonal bipyramid or square pyramid. Although the major trends follow those set forth by Rossi and Hoffmann,¹³ the d^9 configuration provides an exception.

It is generally found⁸ that square-pyramidal copper(II) complexes have apical bonds that average about 0.35 Å longer than basal central atom-ligand distances. The difference between bond lengths that can be classified as equatorial relative to those that are axial for the trigonal-bipyramidal structural type for copper(II) complexes is about 0.15 Å, with the equatorial bonds having the greater length.

Pentacoordinated d^8 low-spin nickel(II) complexes follow the same pattern.⁸ For these nickel(II) complexes containing like ligands, however, the differences are smaller. The nickel complexes exhibiting axial-equatorial character of the trigonal bipyramid over the observed spectrum of structural distortions (Figures 2 and 3) have nickel-ligand equatorial distances which average about 0.05 Å longer than the respective axial distances. Apical distances in the square pyramid are approximately 0.2 Å longer than nickel-ligand basal distances. Bond distance data⁸ for high-spin nickel(II) square pyramid show slightly longer basal bonds relative to apical bonds, averaging a few hundredths of an angstrom longer.

While it is expected¹³ that d^8 low-spin five-coordinated complexes follow the observed pattern for relative bond lengths in the two geometrical types, d^9 complexes should follow this pattern to a lesser degree, not to a greater degree as observed for copper(II). Possibly, the addition of an electron to the $SP\ b_1$ level, which is strongly metal-basal ligand antibonding, serves to lengthen the apical copper-ligand bond rather than to decrease the trans basal angle θ . This could occur if the $x^2 - y^2$ orbital mixes in an antibonding way with basal ligand orbitals for copper complexes and as a consequence results in a destabilization of the b_1 level and hybridization away from the basal ligands toward the apical site. With considerable basal π bonding for copper complexes enhancing bond electron pair repulsions, this would rationalize the high θ value maintained for square-pyramidal copper(II) complexes (Figure 7).

As a final point, both the θ distortion coordinates and the dihedral angle coordinates suggest that the concerted axial-equatorial bending process is a predominant feature in assessing molecular distortions for five-coordinated derivatives. Further, the ease of distortion along these coordinates, whether by relief of ligand ring strain, steric effects, particular electronic properties of ligands, or lattice effects, implies that they represent a basis for stereochemical nonrigidity prevalent in solution for some five-coordinated members. Although structures of transition-metal derivatives tend to concentrate more readily toward the square pyramid for many of the elements, particularly d^6 complexes, there is a distribution covering the range between the two idealized limits in most cases. The preference of low-

spin d^6 complexes for the square pyramid is supported by both the angular overlap model¹² and the relative ordering of energy levels in Figure 8.¹³

ACKNOWLEDGEMENT

The support of this research by the National Science Foundation (CHE 8205411) is greatly appreciated. I am extremely grateful to Professor Roberta O. Day and Joan M. Holmes, who carried out the calculations on structural distortions.

REFERENCES AND NOTES

1. Pentacoordinated Molecules. 55. Previous paper in the series: Deiters, J. A.; Holmes, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 3307–3309.
2. Holmes, R. R. *ACS Monogr.* **1980**, *175*, 44.
3. Zemmann, J. Z. *Anorg. Allg. Chem.* **1963**, *324*, 241.
4. Holmes, R. R.; Deiters, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 3318.
5. Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933.
6. See ref 2, Chapter 3.
7. Orioli, P. L. *Coord. Chem. Rev.* **1971**, *6*, 285.
8. Holmes, R. R. *Prog. Inorg. Chem.*, in press.
9. Holmes, R. R. *Acc. Chem. Res.* **1979**, *12*, 257.
10. Muetterties, E. L.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1974**, *96*, 1748.
11. This analysis is given in full in ref 8.
12. Purcell, K. F.; Kotz, J. C. "Inorganic Chemistry"; Saunders: Philadelphia, 1977; p 587 ff.
13. Rossi, A. R.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 365.