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Similarities in the Structural Chemistry of d^8 and d^9 Transition Metal Complexes. An Explanation in Terms of the Angular Overlap Model

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Using a simple angular overlap model described previously the stabilization energies of square-planar, square-pyramidal, and octahedral d^8 and d^9 complexes are found to be equal when ligand–metal d-orbital interactions only are included. This implies that the bond energies between the metal and the fifth and sixth ligands are low. This is found to be the case in practice, but only a few of the observed distortions may be rationalized by the Jahn–Teller formulation.

Introduction

We have recently shown[1,2] that the orbital stabilization energy of a transition metal complex relative to that of the free metal atom or ion plus ligands is partly determined by the overlap integrals, S, between the empty d orbitals and the ligands. Specifically $\sum(\sigma)$ the total σ stabilization energy arising from interaction between the metal d orbitals and the ligands may be written approximately as

$$\Sigma(\sigma) = \beta_\sigma \sum_j h_j S^2 [(\mathrm{d}(\Gamma_j); \sigma(\Gamma_j)] \qquad (1)$$

where h_j is the number of one-electron holes in the set of d orbitals transforming under the irreducible representation Γ_j of the molecular point group. This particular equation derived from the angular overlap model[2,4] of metal–ligand interaction represents the forces between the holes in the central metal electronic charge distribution and the ligand σ pairs. It is a remarkably simple one to handle and has already shown its potential in predicting the geometries of binary transition metal complexes.[1] β_σ is a parameter dependent upon the nature of the ligand and in the absence of π-bonding effects increases with increasing field strength. In this paper we shall consider the application of eq 1 to the special case of low-spin d^8 and d^9 complexes where the only contribution to $\sum(\sigma)$ arises from ligand overlap with the highest energy d orbital

$$\Sigma(\sigma) = k\beta_\sigma S^2(\mathrm{d}; \sigma) \qquad (2)$$

$$h_j = k = 1\ (d^9), 2\ (d^8)$$

The most stable angular geometries predicted by eq 2 for three-, four-, five-, and six-coordinate species with the 22220 d-orbital electronic configuration are[1] respectively the C_{2v} (T), D_{4h} (square planar), C_{4v} (square pyramidal), and O_h (octahedral) structures. For the five-coordinate species the trigonal bipyramid is calculated to be less stable but very close in energy to the square pyramid, and the two are readily interconverted. Three-coordinate d^8 and d^9 complexes are unknown but many examples of the higher coordination numbers are known.

Energies of the Structures

For the C_{2v}, D_{4h}, C_{4v}, and O_h geometries above, the highest energy d orbital is $d_{x^2-y^2}$ and the overlap integral S between this orbital and the ligand group orbital of the same symmetry for insertion into eq 1 may be readily calculated. For the D_{3h} three-coordinate geometry the ligand σ molecular orbital (ϕ) of the same symmetry species (e′) as $d_{x^2-y^2}$ (the plane of the molecule lies in the xy plane) may be written

$$\phi_{x^2-y^2} = \frac{1}{6^{1/2}}(2\sigma_1 - \sigma_2 - \sigma_3)$$

The σ_i's represent ligand σ orbitals pointing at the central metal. The overlap integral of $\phi_{x^2-y^2}$ with $d_{x^2-y^2}$ is found to be $((3/2)2^{1/2})S_\sigma$ where the parameter S_σ is the overlap of a ligand σ orbital lying along the z axis with the d_{z^2} orbital. Similarly for the orthogonal four-, five-, and six-coordinate structures the required overlap integral arises *via* overlap of the function (of species b_1)

$$\phi_{x^2-y^2} = \frac{1}{2}(\sigma_1 + \sigma_2 - \sigma_3 - \sigma_4)$$

with $d_{x^2-y^2}$ (σ_1–σ_4 represent the ligand σ orbitals lying in the xy plane) and is simply evaluated as $3^{1/2}S_\sigma$. (The overlap of an in-plane ligand σ orbital directed along the x or y axis with one lobe of $d_{x^2-y^2}$ is $(3^{1/2}/2)S_\sigma$). Using these values $\sum(\sigma)$ for the three-, four-, five- (SPY), and six-coordinate structures are easily shown to be $1.125k\beta_\sigma S_\sigma^2$, $3k\beta_\sigma S_\sigma^2$, $3k\beta_\sigma S_\sigma^2$, and $3k\beta_\sigma S_\sigma^2$. For the TBP structure, the highest energy d orbital is d_{z^2}, and

$$\phi_{z^2} = \frac{1}{11^{1/2}}(2\sigma_1 + 2\sigma_2 - \sigma_3 - \sigma_4 - \sigma_5)$$

where the labels 1 and 2 refer to the axial ligands and 3–5 to the equatorial ligands. The overlap integral of this function with d_{z^2} (the overlap of σ_3, σ_4, and σ_5 with the collar of d_{z^2} is $^1/_2 S_\sigma$) is $(11^{1/2}/2)S_\sigma$. Thus for this geometry $\sum(\sigma) = 2.75k\beta_\sigma S_\sigma^2$. The value of $\sum(\sigma) = 3k\beta_\sigma S_\sigma^2$ calculated for the square-pyramidal five-coordinate structure is for a geometry where the metal–ligand bonds are all orthogonal. In practice any such geometry will distort such that the four equatorial metal–ligand bonds droop away from the xy plane and away from the axial ligand. In this case $\sum(\sigma) = 3k(\cos^4\theta)\beta_\sigma S_\sigma^2$ where θ is the droop angle from the orthogonal structure. The SPY and TBP structures become isoenergetic for $\theta \approx 12°$. For the d^6 system with d-orbital occupation numbers 22200 the values of $\sum(\sigma)$ for square-planar, square-pyramidal, and octahedral structures are $8\beta_\sigma S_\sigma^2$, $10\beta_\sigma S_\sigma^2$, and $12\beta_\sigma S_\sigma^2$, respectively.

Relationship between Four-, Five-, and Six-Coordinate Species

The most interesting piece of information contained above is that there is no calculated energy difference between the square-planar, idealized square-pyramidal, and octahedral geometries for low-spin d^8 and d^9 systems. This means that the energy of attachment of the fifth ligand to the square-planar structure is zero and similarly that the attachment of two ligands to the four-coordinate geometry is zero. In both cases the proviso exists that in the SPY and octahedral structures so formed the $d_{x^2-y^2}$ orbital has no other d orbital to higher energy. By way of contrast, addition of an extra ligand to the square or square-pyramidal structures for the low-spin d^6 configuration leads to an increase in stabilization energy of $2\beta_\sigma S_\sigma^2$ in each case. In practice, therefore, we surmise that any energy change occurring in these processes will be small. More specifically, the bond energy associated with metal–equatorial ligand interactions remains unchanged on addition of the fifth and sixth ligands. That for central metal atom–axial ligand interaction is identically zero in the

Table I. Some Examples of Bond Lengths (Å) in Cu^{II} (d^9) Systems

$CuCl_2$	4 Cl at 2.30, 2 Cl at 2.95
$CsCuCl_3$	4 Cl at 2.30, 2 Cl at 2.65
$CuCl_2 \cdot 2H_2O$	2 O at 2.01, 2 Cl at 2.31, 2 Cl at 2.98
$CuBr_2$	4 Br at 2.40, 2 Br at 3.18
CuF_2	4 F at 1.93, 2 F at 2.27
K_2CuF_4	2 F at 1.95, 4 F at 2.08

octahedral and idealized square-pyramidal geometries since these axial ligands have no overlap with the $d_{x^2-y^2}$ orbital. (In the SPY structures with nonzero droop angles, the axial ligand–central atom bond energy will still be zero provided that $d_{x^2-y^2}$ remains the highest energy d orbital.) There is a wealth of experimental evidence supporting our proposals, some of it rationalized under the disguise of the Jahn–Teller effect but most of it unexplained on a general basis.

First, for d^9 systems the ideal octahedral geometry with an electronic configuration $(t_{2g})^6(e_g)^3 = {}^2E_g$ is predicted to be Jahn–Teller unstable. The Jahn–Teller "active" vibrational mode is of species e_g and this would give rise to a tetragonally distorted structure, either with four short (equatorial) and two long (axial) metal–ligand bonds or *vice versa*. In contrast to other Jahn–Teller unstable systems (high-spin Cr^{II} and Mn^{III}), which we discuss below, the axial bond lengths in the Cu^{II} systems range from being very short (sometimes shorter than the equatorial ones) to being very long (Table I). The equatorial bond lengths are generally similar in all complexes. As a result it is often impossible to distinguish between four- (square planar), five- (square pyramidal), and six-coordination (octahedral) in these systems. A much smaller range of axial bond lengths is seen in Cr^{II} and Mn^{III} systems and always the axial bond length is longer than the equatorial. These species are best described as tetragonally distorted six-coordinate octahedral systems. The Cu^{II} examples are often quoted as being "classic" examples of Jahn–Teller distortions, but, similar large distortions are also seen in the structure of $CuCl_2 \cdot 2H_2O$ where two oxygen atoms lie at 2.01 Å, two Cl atoms at 2.31 Å, and two more Cl atoms at 2.98 Å. Here the environment of the central Cu^{II} ion is not a regular octahedron (due to the nonequivalence of the ligands) and the orbital degeneracy of the ground electronic state seen for the nonhydrated $CuCl_2$ is lost. It is thus technically incorrect to claim that the distorted $CuCl_2 \cdot 2H_2O$ structure is due to Jahn–Teller effects. Distorted octahedral structures are also found for similar Ag^{II} compounds. For square-pyramidal d^9 complexes similar differences between axial and equatorial bond lengths are also seen however. For example, in the dimeric *N,N'*-disalicylideneethylenediaminecopper(II) complex[5] the axial bond length is 2.41 Å and the equatorial bond length 2.01 Å. For diaquoacetylacetonatecopper(II) picrate these bond lengths are 2.76 and 1.88 Å, respectively. For these species the Jahn–Teller theorem cannot be invoked. In the C_{4v} point group $d_{x^2-y^2}$ and d_{z^2} are nondegenerate and the difference in energy between them may be shown to be $\beta_\sigma S_\sigma^2$ by using the angular overlap model. The ground electronic state is therefore not orbitally degenerate. Since the approach of the axial ligands is a very low-energy process the Cu^{II}–axial ligand bond length should be determined predominantly by crystal forces and should thus show wide variations, as is observed. The equatorial bond lengths on the other hand should be determined by overlap forces and should vary little from one environment to another for a given ligand. This is observed. The vast majority of the Cu^{II} complexes contain (Table I) four short (normal) equatorial bonds and two long axial bonds (one for the SPY structure). In a few situations four short (normal) equatorial bond lengths are found plus the slightly shorter axial bond lengths. From the Jahn–Teller description of the latter examples we expect to see two short axial bonds and four long equatorial bonds, a situation which is not observed. The Jahn–Teller theorem, while providing a tool to rationalize some situations is lacking in general applicability while the approach used in this paper provides a ready route to the rationalization of these phenomena. A summary of the structural results concerning the axial ligands in d^9 (Cu^{II}) systems is given by Hathaway.[7] It is noted here that the weak axial bonds are not in accord with the size of the metal d_{z^2}–ligand overlap integrals, which on the present model, concerned with overlap of ligand orbitals with the empty metal d orbital, is an irrelevant consideration. Hathaway concluded that the experimental data are best explained in terms of the prolate ellipsoid idea of Gillespie which as mentioned elsewhere[1] is not a concept of universal applicability.

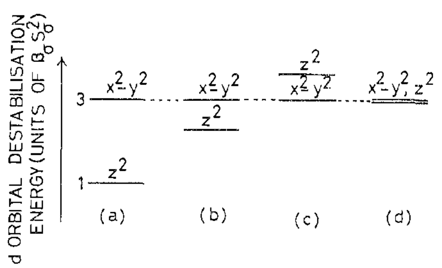

Figure 1. Orbital destabilization energies of the $d_{x^2-y^2}$ orbitals in different environments: (a) square plane; (b) octahedral situation where the two axial ligands have a weaker σ interaction with the metal than the equatorial ones; (c) octahedral situation where the two axial ligands have a stronger σ interaction with the metal than the equatorial ones; (d) true octahedron with all ligands identical.

For low-spin d^8 complexes the relationship between these structures is very similar. The equilibrium

$$NiL_4 + 2L' \rightleftharpoons trans\text{-}NiL_4L'_2$$

between a diamagnetic square-planar NiL_4 unit and the *trans*-L'_2 octahedral structure lies to the left unless the L' are good σ donors when pure crystalline six-coordinate compounds may be isolated. This is the well-known "anomalous" behavior of square planar Ni^{II} complexes as typified by Lifschitz's salts, where two axial ligands may be weakly bound to the square-planar unit. (In the copper case similar equilibria are less well-defined but do exist.[8]) In the d^8 case, however, the Jahn–Teller effect cannot be invoked to explain this tetragonal distortion. The $(t_{2g})^6(e_g)^2$ high-spin electronic configuration of the octahedral geometry gives rise to an orbitally nondegenerate electronic ground state (${}^3A_{2g}$). In several cases the four-coordinate complexes polymerize to give species containing Ni^{II} in five- and six-coordinate environments, *e.g.*, nickel acetylacetonate. The position of equilibrium (and thus concentration of monomers, dimers, etc.) is generally complex, being temperature and concentration dependent, and is indicative of low-energy pathways connecting square-planar four-, square-pyramidal five-, and octahedral six-coordinate Ni^{II}. The resemblance to the behavior noted above in structural Cu^{II} chemistry is very apparent.

The increasing tendency for the equilibrium above to lie to the right for good σ-donor ligands L' is another experimental feature approachable on the model. For the square-planar arrangement ML_4 $d_{x^2-y^2}$ and d_{z^2} have destabilization energies of $3\beta_\sigma S_\sigma^2$ and $\beta_\sigma S_\sigma^2$, respectively (Figure 1a). For the regular octahedral situation ML_6 where all the ligands are equivalent these destabilization energies are both equal to $3\beta_\sigma S_\sigma^2$ (Figure 1c). For the situation where the axial and equatorial ligands are different the energies of the d orbitals appear as in Figure 1b and d. If we distinguish between the parameters for equatorial and axial ligands and rewrite eq 2 as

$$\Sigma(\sigma) = 2\sum_{\substack{\text{all}\\\text{ligands}}} \beta_\sigma(X) S_\sigma^2(X\sigma; d) \qquad (3)$$

the total destabilization of the d_{z^2} orbital is simply given by

Table II. Bond Lengths in TBP Five-Coordinate d^8 and d^9 Structures

	Lengths, Å		
	Axial	Equatorial	Ref
$Ni(CN)_5{}^{3-}$ (d^8)	1.838 (9)	1.94[a]	10
$Co(CNCH_3)_5{}^+$ (d^8)	1.84 (2)	1.88 (2)	11
$Fe(CO)_5$ (d^8)	1.810 (3)	1.833 (2)	12
$CuCl_5{}^{3-}$ (d^9)	2.2964 (12)	2.3912 (13)	13
$CuBr_5{}^{3-}$ (d^9)	2.4500 (22)	2.5191 (17)	14

[a] Average of several slightly nonequivalent Ni–C bonds.

$\beta_\sigma(L)S_\sigma{}^2(L) + 2\beta_\sigma(L')S_\sigma{}^2(L')$. The $d_{x^2-y^2}$ orbital is exclusively concerned with the equatorial ligands and has a destabilization energy of $3\beta_\sigma(L)S_\sigma{}^2(L)$. For Figure 1b the axial ligands have a smaller interaction with the metal than the equatorial ones and the stabilization energy of the structure $\sum(\sigma) = 6\beta_\sigma S_\sigma{}^2$. In Figure 1c the axial ligands have a larger interaction with the metal than the equatorial ones and $\sum(\sigma) > 6\beta_\sigma S_\sigma{}^2$ since the orbital involved in eq 2 is the d_{z^2} orbital, now of highest energy. In the arrangement of Figure 1c therefore the octahedral *trans*-L'_2 structure may be stabilized with respect to the square-planar one. For the d^6 system of course, addition of the two axial ligands results in a more stable structure and it is noteworthy that for the heavier members of the Ni group there are few octahedral complexes of d^8 Pt^{II} or Pd^{II} but a wealth of examples of octahedrally coordinated d^6 Pd^{IV} and especially Pt^{IV} d^6 systems.

For five-coordinate d^8 complexes there is a sizable amount of data on both low- and high-spin square-pyramidal systems.[9] In all low-spin examples the axial bond length is elongated compared to the equatorial. For example in $Ni(CN)_5{}^{3-}$ the equatorial Ni–C length is 1.80 Å and the axial 2.17 Å. However no such elongation is observed at all in high-spin complexes. This is just what is expected from eq 1. With equal occupation 22211 (high spin) of the two d orbitals involved in σ bonding (such that the equatorial and axial bonds are equally favored) no bond length difference is seen. With unequal occupation 22220 (low spin) of these two orbitals (such that the d orbital–axial ligand interaction is zero) axial elongations are observed.

A few five-coordinate TBP d^8 and d^9 structures are known containing identical ligands. In all of them the axial and equatorial bond lengths are very close (Table II). In the last two examples conclusive proof was obtained that the axial bond lengths were shorter than the equatorial ones. In the other examples the difference is little more than a standard deviation or so. This may be rationalized by breaking eq 2 into contributions from axial and equatorial ligands as

$$\Sigma(\sigma) = k(2\beta_\sigma(\mathrm{ax})S_\sigma{}^2(\mathrm{ax}) + {}^3/_4\beta_\sigma(\mathrm{eq})S_\sigma{}^2(\mathrm{eq}))$$

This implies that the bond energy between an axial ligand and the metal is 4 times the corresponding parameter for an equatorial ligand. Thus the equatorial bonds should be longer than the axial ones as is observed.[15] For the low-spin d^4 system however a similar calculation shows axial and equatorial bond energies to be equal. We have no example to prove this point but there is no reason why the situation should not be similar to the regular octahedral $Cr(CO)_6$ system.

High-Spin Cr^{II} and Mn^{III}

Distortions ascribed to Jahn–Teller effects are also observed for low-spin Ni^{III} (22210) and high-spin Cr^{II} and Mn^{III} (11110) species. Here there is a single electron hole in the second highest d orbital and thus the summation of eq 1 extends over the two highest d orbitals (if we are considering purely σ-bonding effects in structures containing orthogonal arrangements of ligands). The total stabilization afforded by the d_{z^2} orbital in an octahedral structure is calculated *via* evaluation of the relevant overlap integral

$$\phi_{z^2} = \frac{1}{12^{1/2}}(2\sigma_1 + 2\sigma_2 - \sigma_3 - \sigma_4 - \sigma_5 - \sigma_6)$$

(where the labels 1 and 2 refer to axial (z) ligands and 3–6 refer to equatorial ligands). We find that the total σ stabilization from eq 1 for the configuration (···10) associated with the equatorial ligands is $7\beta_\sigma S_\sigma{}^2$ ($1.75\beta_\sigma S_\sigma{}^2$ per ligand). For the axial ligands the total stabilization is $2\beta_\sigma S_\sigma{}^2$ ($\beta_\sigma S_\sigma{}^2$ per ligand) indicating stronger equatorial bonds relative to the axial ones. Ample data exist to show that distortions occur in these systems and that they take the form of *elongation* of the octahedron along one axis. However, these distortions are never as extreme as the ones observed for the Cu^{II} case, and the situation is strikingly different from that of Cu^{II}.

For the d^4 species the stabilization energy associated with the axial ligands is nonzero but less than that for the equatorial ones. The axial bond length should always then be greater than the equatorial. Only in Cu^{II} where the axial bond energies are zero should there be virtually no restriction (qualified by the presence of large repulsive forces at small metal–ligand distances) on the axial bond length so that four-, five-, and six-coordination may sometimes be almost indistinguishable. For low-spin d^6 (22200) species where holes appear symmetrically in the top two orbitals a similar calculation to the one above shows that the equatorial ligand stabilization is equal to the axial ($2\beta_\sigma S_\sigma{}^2$ per ligand). $Cr(CO)_6$ with this configuration is a regular octahedron.

Inclusion of Other Orbitals

π interaction in the orthogonal ligand structures (square planar, SPY, and octahedral) involves only the d_{xy}, d_{xz}, and d_{yz} orbitals (taking the z axis to be coincident with the fourfold axis). Thus the high-lying $d_{x^2-y^2}$ orbital is not concerned with π-bonding effects. Since for π-donor ligands (where the ligand π orbital lies deeper than the metal d orbitals) in the d^8 and d^9 cases both M–L π-bonding (predominantly ligand π) and π-antibonding orbitals (predominantly metal d_{xy}, d_{yz}, or d_{xz}) are completely filled $\sum(\pi) = 0$ for all three structures. For the case of π acceptors however $\sum(\pi)$ can be readily shown to be $16\beta_\pi S_\pi{}^2$, $20\beta_\pi S_\pi{}^2$, and $24\beta_\pi S_\pi{}^2$ for the three structures respectively. (This is simply $4n\beta_\pi S_\pi{}^2$ where n is the number of π-bonding ligands each containing two π orbitals. If each ligand contains only one usable π orbital this figure must be halved.) Here the M–L π-bonding orbitals are occupied and the antibonding orbitals are unoccupied. S_π is the overlap integral between a ligand π orbital located along the z direction and lying in the xz plane and a metal d_{xz} orbital. (Here we are assuming for the sake of convenience that the ligands extra to the square plane are identical with the four already present. If the additional ligands are different, then we can readily see that the stabilization afforded by π bonding on increase of coordination number by 1 is simply $4\beta_\pi' S_\pi'^2$ where the primed parameters refer to the additional ligand.) Similarly for a trigonal-bipyramidal structure since the highest energy d orbital is not involved in π bonding, $\sum(\pi) = 20\beta_\pi S_\pi{}^2$ for five identical π-acid ligands. Thus axial ligands which are π acids should be the most favorable candidates for the observation of SPY structures of d^8 and d^9 systems. Square-pyramidal $Ni(CN)_5{}^{3-}$ mentioned above fulfills this criterion.

An extra stabilization term in eq 1 also arises if (n + 1)s and (n + 1)p orbitals are included on the metal and, provided none of the (predominantly) metal s or p orbitals are occupied, will always exert a stabilizing effect on any metal–ligand bonding. From the experimental data concerning the weak attachment of ligands to the fifth and sixth sites, we conclude that these terms are small and are of secondary importance.

The Jahn–Teller Theorem

The Jahn–Teller theorem applies to orbitally degenerate electronic states only. Since in every case such degeneracy also corresponds to an asymmetric arrangement of one-electron holes in the high-energy d orbitals, both Jahn–Teller requirements and the forces of eq 1 demand a distorted structure. However eq 1 holds for *all* transition metal complexes irrespective of the nature of the electronic state and in fact, subject to the restrictions of the Pauli principle, is independent of the total spin multiplicity of the system (*i.e.*, the *orbital* energy of a complex with electronic configuration (···11) is independent of whether these electrons are spin paired or not). However, in addition to arriving at distorted structures for Jahn–Teller unstable systems, the present approach is able to consider the stereochemistry of species which cannot use the theorem as an excuse to distort. In our previous work on the angular geometry of transition metal complexes[1] using eq 1 we found that Fe(CO)$_3$ ($^3A_2$) was predicted and observed to be a pyramidal molecule whereas there was no reason under the Jahn–Teller scheme for the geometry to distort from planar. Similarly in our quantitative molecular orbital calculations (using the Wolfsberg–Helmholtz approximation, closely related to the overlap integral determined stabilization energy of eq 1) on binary transition metal carbonyls[2] it was found that orbital energy changes on distortion, in addition to Jahn–Teller considerations, were required to rationalize the computed equilibrium geometries. Although we do not deny the existence of marked vibronic effects which have been well documented in some metal hexafluorides for example (dynamic Jahn–Teller effect), there are considerable misgivings about the utility of Jahn–Teller arguments to rationalize transition metal structures.

The angular overlap model on the other hand is a relatively crude simplistic approach. We have deliberately ignored interactions with s and p orbitals on the metal which are of course responsible for holding d^{10} complexes together and have left out any dependence of overlap integral on metal–ligand bond length. With regard to the latter comment, our arguments therefore strictly hold only for an idealized arrangement where all M–L bond lengths are equal. The model therefore may only faithfully represent gross structural effects. At its present stage of development we do not look to it for the finer details of molecular geometry. Its overwhelming advantage is that it is a simple, easy-to-use way (and at present the only method of universal applicability) of looking at the salient structural features of transition metal complexes.

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(15) The situation is of course not quite as simple as this since in the d^{10} complex CdCl$_5^{3-}$ the axial bond lengths are slightly shorter (2.527 (5) Å) than the equatorial ones (2.564 (5) Å: T. V. Long, A. W. Herlinger, E. F. Epstein, and I. Bernal, *Inorg. Chem.*, **9**, 459 (1970)). However these authors pointed out that the axial "compression" in CuCl$_5^{3-}$ compared to CdCl$_5^{3-}$ is of electronic origin (as we claim here) and not due to crystal effects.

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Photoelectron Spectroscopy of *closo*-Carboranes. Observation of Exo-Polyhedral Molecular Orbitals

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The He(I) photoelectron spectra of 1,5-dicarba-*closo*-pentaborane(5), 1,6-dicarba-*closo*-hexaborane(6), 2,4-dicarba-*closo*-heptaborane(7), and 1,7-dicarba-*closo*-icosaborane(12) are reported. It is shown that the spectra of these molecules provide experimental justification for a theoretically predicted separation of the molecular orbitals of these species into exo- and endo-polyhedral types. In addition, it is pointed out that ionization from certain exo-polyhedral orbitals results in bands with empirically recognizable characteristics. Finally, the photoelectron spectrum of pentaborane(9) indicates that the exo–endo separation is valid for the boranes as well.

There have been a number of successful approaches to a systemization of the chemistry of the boranes and heteroboranes. These range from empirical approaches based on reaction chemistry[1] or synthesis[2] to theoretical approaches based on topological rules.[3] On the theoretical side, a valence-bond treatment with localized three-center and two-center bonds gives a generally adequate and conceptually useful description of the bonding for nido or arachno (open) structures. However, the highly interconnected structures and delocalized bonding of the *closo*-boranes and heteroboranes are only fruitfully treated with molecular orbital methods.[3] These approaches, although conceptually more complex, have been used to rationalize sites of substitution *via* various calculations of charge distributions.[4] In addition, calculations of this type have given insight into rearrangement pathways[5] while localization routines applied to SCF calculations have been used to test the idea of a localized three-center bond.[6]

Of more pertinence to this work is the conclusion of a molecular orbital study of Hoffmann and Lipscomb.[7] In order to obtain better insight into the nature of the structure and bonding of *closo*-boranes, they investigated simplifications of the complete molecular orbital picture. In fact, they examined various ways of factoring the secular equation and, by comparison of factored and unfactored results, it was concluded that orbitals that point out from the polyhedral framework and which are involved in heavy-atom hydrogen interactions are separable from those involved in bonding the framework atoms. This factorization, which is formally analogous to the σ–π separation in organic systems, predicts that in a polyhedral borane or heteroborane with N heavy atoms there will be N molecular orbitals that are exo-polyhedral bonding and endo-polyhedral nonbonding in character. This idea has been generally accepted as exemplified in a recent proposal for the systemization of borane and heteroborane chemistry in terms of "magic" numbers of electrons which explicitly excludes the electrons involved in exo-polyhedral bonds.[8]