Table I. Stability Constants for Formation of ML (K_1) and ML_2 (K_2) in Water at 25°[a]

		DOP	DPM	NH_3
Cu^+	$\log K_1$	12.60		5.93
	$\log K_2$	7.74		5.93
Ag^+	$\log K_1$	11.53		3.39
	$\log K_2$	9.02		3.92
Hg^{2+}	$\log K_1$		14.3	8.8
	$\log K_2$		10.3	8.7
Cd^{2+}	$\log K_1$	3.94	0.90	2.65
	$\log K_2$	3.75	2.48	2.10

[a] DOP = $P(C_2H_5)_2(C_2H_4OH)$; DPM = $P(C_6H_5)_2(C_6H_4SO_3)^-$. Data from ref 15.

with monodentate phosphine and ammine ligands.[15] For the first three metal ions, which should form linear bis complexes, there is obviously a reluctance to add the second phosphine ligand, but not the second ammine ligand. Cadmium ion, which should form a pseudotetrahedral complex, does not show this antisymbiotic behavior.

Cobalt(III) is a metal ion subject to symbiotic effects. For example, the corrin ring or porphyrin rings as cis ligands convert the normally hard Co(III) center into a relatively soft center. However, an alkyl group attached to cobalt in these complexes has an antisymbiotic effect on the position trans to it.[16]

A great deal of rate data on platinum(II) complexes has been accumulated.[14,17] A very strong symbiotic effect is found in the rates when soft ligands are in the cis position to the leaving group. Thus *trans*-$Pt[P(C_2H_5)_3]_2Cl_2$ reacts very slowly with hard bases and very rapidly with soft bases, compared to *trans*-$Pt(py)_2Cl_2$. The same is true for Pt(bipy)SCNCl, compared to $Pt(bipy)Cl_2$. However, *trans*-$Pt(py)_2CH_3Cl$ shows an antisymbiotic effect.[18]

Metal carbonyls of the formula $M(CO)_nL$, where $n = 4$ or 5, are activated toward substitution when L is a halogen or an N or O atom donor but not when L is a C, S, P, or As atom donor.[19] This behavior represents a normal symbiotic effect, the complex containing mixed hard and soft ligands being destabilized. However it is always a CO group trans to another CO group which is replaced.

An examination of the structures of transition metal hydrides shows a remarkably consistent pattern of behavior.[20] There are some hundreds of structures available for compounds of the general formula $ML_l(CO)_mX_nH_o$ where L is a phosphine or arsine and X is a halogen or an O- or N-type donor ligand. With only two or three exceptions, all hydrides are cis to each other and not trans. H and CO usually avoid being trans to each other. The relatively hard ligand X is always trans to either H or CO and never trans to L, unless $n > 1$. The same pattern of behavior is found for alkyl complexes of the heavier transition metals.[21]

We can understand these structural features in terms of the instability of two soft ligands trans to one another, if the order of decreasing softness is $R^-, H^- > CO > L > X$. The structures of the adducts formed when H_2, RX, HX, etc., undergo oxidative addition to $IrL_2(CO)X$ and related molecules are also seen to fall into a logical pattern.[22]

Antisymbiotic behavior has been related in the previous examples to the operation of trans influences. It is well known that the trans effect diminishes in ascending a group in the periodic table. Thus *trans*-dialkyl or -diaryl complexes are quite rare for Pt(II) and more common for Pd(II) and Ni(II).[21b] The rule of mutual destabilization of two soft ligands trans to one another is weaker for the first transition series than for the third. This shows up in the structures of chelates containing S and O donors, or S and N donors, as mentioned earlier.

The trans influence is undoubtedly a result of strong covalent bonding. Thus it is not expected in complexes where the bonding is primarily ionic, as is usually true for class a metal ions.[23] For such metal ions *trans*-dialkyl or -diaryl ligands are common.

Tetrahedral complexes should show diminished antisymbiotic effects, since no true trans positions exist. Nevertheless, a similar competition for orbitals is still present, though diluted. For example, $Cu(NH_3)_2(SCN)$ contains S-bonded thiocyanate, as expected for Cu(I). But Cu(DPPA)(NCS), where DPPA is $(C_6H_5)_2PCCP(C_6H_5)_2$, contains N-bonded thiocyanate.[24]

Finally it should be noted that any factors not included in the simple explanation for symbiosis given initially can also produce opposing effects. These include steric factors, solvation phenomena, and strong ligand to metal π bonding. Such π bonding may account for the fact that symbiosis is very pronounced in organic chemistry (carbon as central atom) but is weak or nonexistent in the remaining group IV elements (Si, Ge, Sn, Pb).[25]

Acknowledgment. This work was partly supported by the National Science Foundation under Grant GP31060X.

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[23] Covalent bonding may also be related to the use of d orbitals, and ionic bonding to the use of p orbitals of the metal, as suggested by Tobias.[6]

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Computer Generation of Cubic Molecular Symmetry Orbitals

Sir:

It is well known that the use of symmetry in molecular orbital studies of moderately large molecules greatly reduces the amount of calculation required and helps to classify the results in a very convenient manner. A starting point in such calculations is the deduction of a basis set of symmetry-adapted linear combination of atomic orbitals (SA-LCAO). Often such a step is accomplished by inspection,[1] sometimes

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[1] (a) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill, New York, N. Y., 1962; (b) C. J. Ballhausen and H. B. Gray, "Molecular Orbital Theory," W. A. Benjamin, New York, N. Y., 1965; (c) F. A. Cotton, "Chemical Applications of Group Theory," 2nd ed, Interscience, New York, N. Y., 1971, Chapter 6.

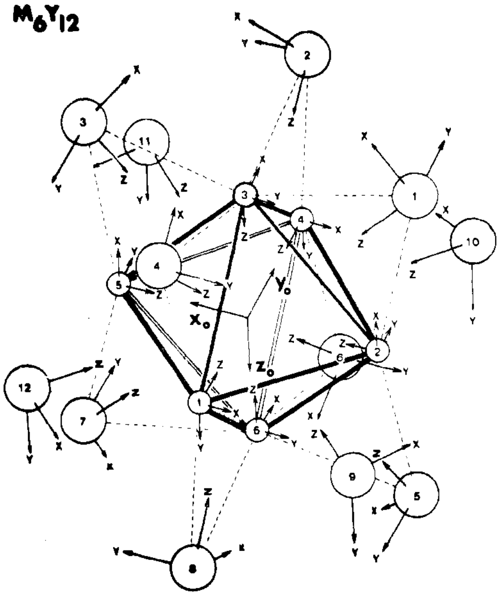

Figure 1. The orientation of the local vectors for M_6 is as in ref 6c. All *z* axes point to the center of the species. The ligand *x* vectors of atoms 1, 2, 3, 4 and 5, 6, 7, 8 point to two common points, respectively, along the fourfold axis formed by metal atoms 3 and 6. Ligand *x* and *z* vectors of atoms 9, 10, 11, 12 lie in the plane formed by metal atoms 1, 2, 4, 5.

involving an unduly large amount of tedious matrix manipulation. In such cases it is appealing to have a digital computer perform these operations and produce a set of "beautified"[2] SA-LCAO basis functions. Such a program has been reported by Chung and Goodman.[2] We offer an alternative computer procedure which, while "very unappealing" to the above authors, is considerably quicker and simpler.[3] Any cubic point group may be handled. More direct advantage is taken of the symmetry properties of the point group.

The procedure proposed by Chung and Goodman involves operating by the rotationally invariant kinetic energy operator, $-\frac{1}{2}\nabla^2$, on the eigenvectors which result from the diagonalization of the atomic orbital overlap matrix. This procedure sorts the symmetry-adapted eigenvectors into the appropriate sets of representations of the point group. For benzene (36 atomic orbitals) the calculation apparently takes about 200 sec on the CDC 3600 computer, about half of which presumably involves the calculation of one- and two-electron integrals.

The procedure proposed in this communication takes a different approach. It essentially parallels the inspection procedure where Wigner[4] projection operators are used. No integrals enter into the problem and the d orbitals are considered with very little additional complication. A character table for the point group *O* is internally supplied, from which the other symmetry tables are deduced. The input involves the atomic positional coordinates (arbitrary scale) and the matrices defining the orientations of the local *x, y,* and *z* vectors in terms of a master coordinate system. A sample calculation is presented on the metal-metal bonded cluster species M_6Y_{12} (Figure 1). Deducing a set of SA-LCAO functions for this species takes less than 10 sec on the UNIVAC 1108 computer.

It is convenient to define all symmetry operators, $\mathbf{S}_j$, in the master basis x_0, y_0, and z_0 (column matrix, $\mathbf{x}_0$) of a coordinate system located at the center of the molecular species. One then defines all the local *m*-center vectors x_m, y_m, and z_m in terms of the master basis

$$\mathbf{x}_m = \mathbf{R}_m\mathbf{x}_0 + \mathbf{t}_m$$

where **R** is a real three-dimensional unitary transformation matrix. The column matrix $\mathbf{t}_m$ defines the translation from the origin of the master system to the origin of the *m*th local coordinate system; that is, it specifies the position of the *m*th atom. To deduce how $\mathbf{x}_m$ changes when $\mathbf{S}_j$ operates on $\mathbf{x}_0$ one can separate the effect of the operator into a translational and a rotational portion. One first considers the translation

$$\mathbf{t}_m' = \mathbf{S}^t{}_j\mathbf{t}_m = \mathbf{t}_n \tag{1}$$

from which one can identify the new center *n*. The superscript t denotes the transpose operation, which arises from the fact that a rotation of $\mathbf{x}_0$ in one sense is equivalent to a rotation of $\mathbf{t}_m$ in the opposite sense with $\mathbf{x}_0$ fixed. Knowing *n*, one proceeds with the rotational portion, *i.e.*

$$\begin{aligned}\mathbf{x}_m' &= \mathbf{R}_m\mathbf{x}_0' \\ &= \mathbf{R}_m[\mathbf{S}_j\mathbf{x}_0] \\ &= \mathbf{R}_m[\mathbf{S}_j(\mathbf{R}^t{}_n\mathbf{x}_n)] \quad (\text{from } \mathbf{x}_n = \mathbf{R}_n\mathbf{x}_0) \\ &= \mathbf{R}_m\mathbf{S}_j\mathbf{R}^t{}_n\mathbf{x}_n\end{aligned} \tag{2}$$

For convenience one can define the $\mathbf{R}_m\mathbf{S}_j\mathbf{R}^t{}_n$ matrix as $\mathbf{M}^j$. Since the p orbitals transform as the *x, y,* and *z* vectors, one has the relation

$$\mathbf{p}_m' = \mathbf{M}^j\mathbf{p}_n \tag{3}$$

If all the local *z* vectors in a *n*-center system ($n > 1$) are radially extended from the center of the molecule, there are no cubic operations that can mix the local *z* vectors with any of the local *x* and *y* vectors. Choosing this orientation, the transformation properties of the orbitals are extensively simplified. The elements m_{13}, m_{23}, m_{31}, and m_{32} vanish and $m_{33} = 1$. Consequently the d orbitals transform in cubic symmetry as

$$\mathbf{d}_m' = \mathbf{N}^j\mathbf{d}_n \tag{4}$$

where $\mathbf{N} =$

$$\begin{bmatrix} 1 & & & & \\ & m_{11}{}^2 - m_{12}{}^2 & m_{11}m_{12} - m_{21}m_{22} & 0 & \\ & m_{11}m_{21} - m_{12}m_{22} & m_{11}m_{22} + m_{12}m_{21} & & \\ & 0 & & m_{11} & m_{12} \\ & & & m_{21} & m_{22} \end{bmatrix}$$

and

$$\mathbf{d} = \begin{bmatrix} d_{z^2} \\ d_{x^2-y^2} \\ d_{xy} \\ d_{xz} \\ d_{yz} \end{bmatrix}$$

The projection operator matrices can be defined as

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(2) A. L. H. Chung and G. L. Goodman, *J. Chem. Phys.*, 56, 4125 (1972).

(3) During the preparation of the manuscript, a search of the literature revealed an excellent report, seldom referenced by inorganic chemists, by S. Flodmark, "On the Theory of Symmetry Projections in Applied Quantum Mechanics," Institute of Theoretical Physics, University of Stockholm, Stockholm (U. S. Army, European Research Office, Contract No. DA-91-591-EUC-2270). It contains a computer program which is produced to derive symmetry functions for atoms in crystals but could be used for deriving molecular functions. The details of the approach used by Flodmark are sufficiently different from that presented in this correspondence to warrant our presentation and discussion.

(4) E. P. Wigner, "Group Theory," Academic Press, New York, N. Y., 1959.

Table I[a]

Coefficients of *metal* SA-LCAO orbitals

Irreducible representation	Orbital type	1	2	3	4	5	6	1′	2′	3′	4′	5′	6′
		Atomic centers											
A_{1g} [A_{2g}]	Z [A]	1	1	1	1	1	1						
A_{2u}	B	1	1	1	−1	−1	−1						
E_g	Z^a, A^a	2	−1	−1	2	−1	−1						
	Z^b, A^b		1	−1		1	−1						
E_u	B^a	2	−1	−1	−2	1	1						
	B^b		1	−1		−1	1						
T_{1g}	$(X, Y)^a$	1			−1				1			−1	
	$(X, Y)^b$		1			−1				−1			1
	$(X, Y)^c$			1			−1	−1			1		
T_{1u} [T_{2u}]	Z^a [A^a]	1			−1								
	Z^b [A^b]		1			−1							
	Z^c [A^c]			1			−1						
	$(X, Y)^a$	1			1					1			1
	$(X, Y)^b$		1			1		−1			−1		
	$(X, Y)^c$			1			1		1			1	
T_{2g}	$(X, Y)^a$	1			−1				−1			1	
	$(X, Y)^b$		1			−1				1			−1
	$(X, Y)^c$			1			−1	1			−1		
	B^a	1			1								
	B^b		1			1							
	B^c			1			1						
T_{2u}	$(X, Y)^a$	1			1					−1			−1
	$(X, Y)^b$		1			1		1			1		
	$(X, Y)^c$			1			1		−1			−1	

Coefficients of *ligand* SA-LCAO orbitals

Irreducible representation	Orbital type	1	2	3	4	5	6	7	8	9	10	11	12
		Atomic centers											
A_{1g}	Z	1	1	1	1	1	1	1	1	1	1	1	1
A_{2g} [A_{2u}]	X [Y]	1	−1	1	−1	1	−1	1	−1	1	−1	1	−1
E_g [E_u]	X^a [Y^a]	2	1	2	1	2	1	2	1	−1	1	−1	1
	X^b [Y^b]		1		1		1		1	1	−1	1	−1
	Z^a	2	−1	2	−1	2	−1	2	−1	−1	−1	−1	−1
	Z^b		1		1		1		1	−1	−1	−1	−1
T_{1g} [T_{1u}]	X^a [Y^a]	1		−1		−1		1					
	X^b [Y^b]		1		−1		−1		1				
	X^c [Y^c]									1	1	1	1
	Y^a [X^a]	2	1		1		−1	−2	−1	−1	1	1	−1
	Y^b [X^b]		3	2	−1	−2	1		−3	−1	−3	1	3
	Y^c [X^c]			1	1	−1	−1			1		−1	
T_{1u}	Z^a	2	1		1		−1	−2	−1	1	1	−1	−1
	Z^b		3	2	−1	−2	1		−3	−3	1	3	−1
	Z^c			1	1	−1	−1				−1		1
T_{2g} [T_{2u}]	Y^a [X^a]	2	−1		−1		1	−2	1	1	−1	−1	1
	Y^b [X^b]		3	−2	−1	2	1		−3	3	1	−3	−1
	Y^c [X^c]			1	−1	−1	1				1		−1
	Z^a	1		−1		−1		1					
	Z^b		1		−1		−1		1				
	Z^c									1	−1	1	−1
T_{2u}	Z^a	2	−1		−1		1	−2	1	−1	−1	1	1
	Z^b		3	−2	−1	2	1		−3	1	−3	−1	3
	Z^c			1	−1	−1	1			1		−1	

[a] The symbolism used here is as follows: A = $d_{x^2-y^2}$, B = d_{xy}, X = p_x or d_{xz}, Y = p_y or d_{yz}, and Z = p_z or s. The primed set of centers occurring for (X, Y) type orbitals refers to Y metal orbitals while the unprimed set refers to the X metal orbitals. The brackets relate isomorphic representations.

$$P_\Gamma = \begin{cases} g/h\sum\limits_j \chi_\Gamma{}^j M^j & \text{for p orbitals} \\ g/h\sum\limits_j \chi_\Gamma{}^j N^j & \text{for d orbitals} \end{cases}$$

where $\chi_\Gamma{}^j$ is a character of the Γth irreducible representation of dimension g for the jth symmetry operation in a point group of order h.

A sufficiently general example should illustrate the method used in the computer program. Consider atomic functions which are composed of the irreducible pairs $\phi_m{}^\alpha$ and $\phi_m{}^\beta$ such as the d_{xz_m} and d_{yz_m} metal orbitals (Figure 1). For a representation of order g the projection of these atomic functions, $\phi_m{}^\mu$, in an n-center system produces $2n$ possible SA-LCAO functions, $\psi_m{}^\mu$. That is

$$P_\Gamma\phi_m{}^\mu = \sum_j^n c_{mj}{}^\mu\phi_j{}^\mu = \psi_m{}^\mu \begin{cases} m = 1, \cdots, n \\ \mu = \alpha, \beta \end{cases} \tag{5}$$

In the $\{\psi_m{}^\mu\}$ set there are only g functions which are linearly independent and form the subset $\{\psi_\sigma'\}$ ($\sigma = 1, \cdots, g$) which spans the Γ representation. For a T type of representation, for example, ψ_1' can be defined as $\psi_1{}^\alpha$ ($\neq 0$). The next member of $\{\psi_\sigma'\}$ is found by projecting another α center, k, such that $\psi_k{}^\alpha \neq \lambda_1\psi_1'$ and thus $\psi_2' = \psi_k{}^\alpha$. The third member must not be a linear construction of ψ_2' and ψ_1'. More centers beyond k are projected until some $\psi_l{}^\alpha \neq \psi_2'\lambda_2 + \psi_1'\lambda_3$ and thus $\psi_3' = \psi_l{}^\alpha$. If projection of $\phi_m{}^\alpha$ yields fewer than g independent functions, projection of $\phi_m{}^\beta$ begins until the subset with g functions is found. In the case of M_6Y_{12}, projection of just one member of the degenerate pair was sufficient to yield proper functions. However, in general, both members of the pair are needed to embody a representation with $g > 1$. At this point the superscript μ may be deleted without loss of clarity.

Suppose $\psi_1' = \Sigma a_i\phi_i$ and $\psi_k = \Sigma b_i\phi_i$ for the second linearly independent function and $\psi_1' = \Sigma a_i\phi_i$, $\psi_2' = \Sigma b_i\phi_i$, and $\psi_l = \Sigma c_i\phi_i$ for the third member (after the second one has been found). For the second member it is assumed, in matrix notation, that $\mathbf{a}\lambda_1 = \mathbf{b}$. For the third member $\mathbf{a}\lambda_3 + \mathbf{b}\lambda_2 = \mathbf{D}\lambda = \mathbf{c}$, where

$$\lambda = \begin{pmatrix} \lambda_3 \\ \lambda_2 \end{pmatrix} \text{ and } \mathbf{D} = \begin{pmatrix} a_1 & b_1 \\ \vdots & \vdots \\ a_n & b_n \end{pmatrix}$$

Solving for the λ's one gets

$$\lambda_1 = \frac{\mathbf{a}^t\mathbf{b}}{\mathbf{a}^t\mathbf{a}} = \frac{\Sigma a_ib_i}{\Sigma a_i{}^2} \tag{6}$$

for the second member and

$$\lambda = (\mathbf{D}^t\mathbf{D})^{-1}\mathbf{D}^t\mathbf{c} = \begin{bmatrix} \dfrac{\Sigma b_i{}^2\Sigma a_ic_i - \Sigma a_ib_i\Sigma b_ic_i}{\Sigma a_i{}^2\Sigma b_i{}^2 - (\Sigma a_ib_i)^2} \\ \dfrac{\Sigma a_i{}^2\Sigma b_ic_i - \Sigma a_ib_i\Sigma a_ic_i}{\Sigma a_i{}^2\Sigma b_i{}^2 - (\Sigma a_ib_i)^2} \end{bmatrix} \tag{7}$$

for the third member. Solutions to (6) and (7) will not exist if ψ_1', ψ_k, and ψ_l are mutually orthogonal to begin with ($\lambda_1 = \lambda_2 = \lambda_3 = 0$) since $\{\psi_\sigma'\}$ is not an empty set. Solution to (7) will not exist if $\det(\mathbf{D}^t\mathbf{D}) = 0$. If solutions to the two relations do exist, they will be either proper or absurd (*reductio ad absurdum*) since *equality* was assumed in the previous paragraph in order to solve for the λ's. One of these two conditions is substantiated by comparing the ratios of the calculated elements for **b** and **c**, *i.e.*, the coefficients of **a** relative to **b** and **D** relative to **c**. If either no solutions exist or the calculated solutions are absurd, then ψ_k and ψ_l qualify to be ψ_2' and ψ_3'.

After the subset is located for a particular representation, it is orthogonalized by the Schmidt procedure (disregarding normalization)

$$\psi^a = \psi_1'$$

$$\psi^b = \psi_2' + k_1\psi_1'$$

$$\psi^c = \psi_3' + k_2\psi_2' + k_3\psi_1'$$

From $\int\psi^{a*}\psi^b\, d\tau = \int\psi^{a*}\psi^c\, d\tau = \int\psi^{b*}\psi^c\, d\tau = 0$ the constants are evaluated (assuming $\int\phi_i^*\phi_j\, d\tau = \delta_{ij}$) in a straightforward manner to be

$$k_1 = -\lambda_1$$

$$k_2 = -\lambda_2 \qquad (8)$$

$$k_3 = -\lambda_3$$

These are either the zero or the "absurd" solutions to (6) and (7).

The species we chose for an example has been studied to varying degrees.[5,6] The figure defines the labeling of the atoms and the orientations of the local vectors. The unnormalized SA-LCAO basis functions are presented in Table I. The functions presented by Haas[6c] and those calculated by the program are identical. In addition, the explicit forms for the $d_{x^2-y^2}$ and d_{xy} symmetry functions are presented here. The ligand functions were not specified by Schneider and Mackay[5] so direct comparison is not possible.

The program we propose is an outcome of the molecular orbital studies we have been performing on the cubic species, Cu_8S_{12}.[7,8] A copy of the computer program (Fortran IV, about 350 cards) is available upon request. Point groups other than cubic can be handled very easily if the program is modified so that the character table is externally supplied.

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[5] R. F. S. Schneider and R. A. Mackay, *J. Chem. Phys.*, 48, 843 (1968), and references therein.

[6] (a) L. D. Crossman, D. P. Olsen, and G. H. Duffy, *J. Chem. Phys.*, 38, 73 (1963); (b) F. A. Cotton and T. E. Haas, *Inorg. Chem.*, 3, 10 (1964); (c) T. E. Haas, Ph.D. Dissertation, Massachusetts Institute of Technology, Cambridge, Mass., Sept 1963.

[7] (a) Presented in part at the Third Central Regional Meeting of the American Chemical Society, Cincinnati, Ohio, June 1971. (b) A complete paper on the MO study of Cu_8S_{12} is in preparation.

[8] L. E. McCandlish, E. C. Bissell, D. Coucouvanis, J. P. Fackler, Jr., and K. Knox, *J. Amer. Chem. Soc.*, 90, 7357 (1968).

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