Molecular Orbital Calculations for an Octahedral Cobalt Carbonyl Cluster Complex, $Co_6(CO)_{14}^{4-}$

By **D. Michael P. Mingos**, Department of Chemistry, Queen Mary College, University of London, Mile End Road, London E1 4NS

Wolfsberg–Helmholtz molecular orbital calculations on an octahedral cluster of cobalt atoms have suggested that the 86 valence electrons in the carbonyl anion $Co_6(CO)_{14}^{4-}$ are all accommodated in bonding and weakly antibonding molecular orbitals and consequently represent a stable closed-shell electronic configuration. The 11 strongly antibonding skeletal molecular orbitals in such compounds have the same symmetries and approximately the same composition as the antibonding orbitals in $B_6H_6^{2-}$ and therefore electron counting schemes based on analogies between boranes and metal clusters are shown to have some validity.

THE geometries and reactivities of many mononuclear and polynuclear transition metal carbonyl and organometallic compounds have been rationalised according to the Inert Gas Rule.[1-3] Octahedral metal carbonyl cluster compounds, *e.g.*, $Rh_6(CO)_{16}$,[4] $Co_6(CO)_{15}^{2-}$,[5]

---

[1] R. S. Nyholm, *Proc. Chem. Soc.*, 1961, 273.

[2] R. Mason, Special Lectures, XXIII, IUPAC Congress, 1971, **6**, 31.

[3] C. A. Tolman, *Chem. Soc. Rev.*, 1972, **1**, 337.

[4] E. R. Corey, L. F. Dahl, and W. Beck, *J. Amer. Chem. Soc.*, 1963, **85**, 1202.

[5] V. Albano, P. Chini, and V. Scatturin, *J. Organometallic Chem.*, 1968, **15**, 423.

$Co_6(CO)_{14}^{4-}$,[6] $Ru_6C(CO)_{17}$,[7] and $H_2Ru_6(CO)_{18}$ [8] are interesting because they cannot be accommodated within the framework of this rule. Each of these molecules (or ions) has 86 electrons in metal–metal or metal–ligand σ-valence orbitals which is two electrons more than that predicted on the basis of the rule.

This failure of the Inert Gas Rule has prompted alternative approaches based either on the molecular orbital or equivalent orbital formalisms. Corey and his co-workers [4] suggested on the basis of a qualitative MO scheme that the additional electron pair in $Rh_6(CO)_{16}$ resides in a weakly antibonding orbital. In contrast Kettle [9] has suggested, using an equivalent orbital approach, that $Rh_6(CO)_{16}$ has a low-lying empty antibonding orbital. The easy formation of $Rh_6(CO)_{16}^{2-}$ (88 valence electrons) or $Rh_6(CO)_{16}^{2+}$ (84 valence electrons) ions are predicted by these models. As only octahedral molecules and ions with 86 valence electrons have been isolated (primarily by Chini and co-workers [5,6]) one must conclude that there is a special stability associated with this number of valence electrons.

More recently Wade [10,11] has indicated an important similarity between octahedral boranes and these transition-metal clusters. In boron hydride polyhedra each B–H fragment can contribute three hybrid orbitals for skeletal bonding and in $B_6H_6^{2-}$ these result in seven very stable skeletal molecular orbitals.[12] He has argued that the metal carbonyl fragment $M(CO)_n$ may also contribute three hybrid orbitals for skeletal binding and form seven stable molecular orbitals in an octahedral cluster. The remaining 36 electron pairs can then be conveniently assigned to metal–ligand or non-bonding orbitals localised on the metal. This electron counting scheme has proved very useful and has been expressed in a general form which is applicable to all carbonyl cluster compounds.[13]

It is not clear, however, why an electron-deficient bonding scheme derived for boranes is applicable to electron-rich transition-metal clusters. Also the basic assumption that only three metal hybrid orbitals form strongly bonding skeletal molecular orbitals is somewhat arbitrary and is not based on any theoretical calculations or experimental observations. This paper reports some molecular orbital calculations which show that 86 electrons do indeed represent a very stable closed-shell configuration for an octahedral arrangement of cobalt atoms and explain the electronic factors responsible for Wade's analogy between boranes and transition-metal clusters.

Details of Calculation.—The $[Co_6(CO)_{14}]^{4-}$ cluster anion is particularly suitable for a molecular orbital calculation because it has idealised O_h symmetry (see Figure 1). Detailed molecular orbital calculations which included both the metal and ligand orbitals as basis functions would be valuable but would require considerable computional time even for this symmetrical ion. Therefore the calculation has been simplified by including only the metal 3*d*, 4*s*, and 4*p* metal orbitals in the calculation. The molecular orbitals most favourably disposed for forming metal–ligand σ-bonds with the bridging and terminal carbonyl ligands can then be evaluated by inspection. A similar technique has been used by Longuet-Higgins and Roberts for octahedral boron anions.[12]

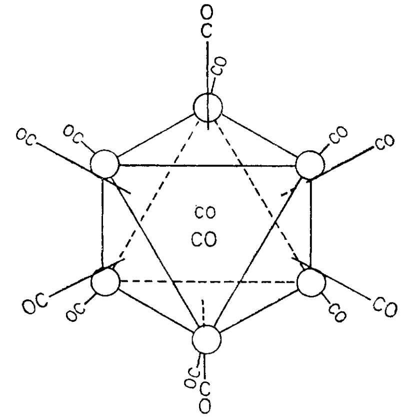


FIGURE 1 Geometry of the $Co_6(CO)_{14}^{4-}$ anion. Each cobalt atom has a terminal carbonyl ligand and eight carbonyls bridge the faces of the octahedron

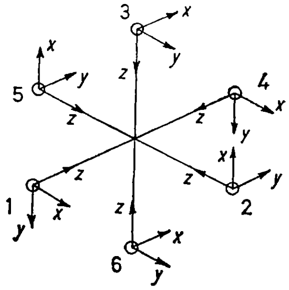


FIGURE 2 Co-ordinate system for the molecular orbital calculation

The co-ordinate system used for the calculation is shown in Figure 2 and is identical to that used by Cotton and Haas [14] for a similar calculation. The transformation properties of the metal *d*, *s*, and *p* orbitals for the point-group O_h are given in Table 1 and LCAO wave functions, ψ_i, with the appropriate symmetry characteristics were constructed by use of standard group-theoretical techniques.[15] The energies, *E*, of the

---

[6] V. Albano, P. L. Bellon, P. Chini, and V. Scatturin, *J. Organometallic Chem.*, 1969, **16**, 461.

[7] A. Singu, M. Bianchi, and E. Benedetti, *Chem. Comm.*, 1969, 596.

[8] M. R. Churchill and J. Wormald, *J. Amer. Chem. Soc.*, 1971, **93**, 5670.

[9] S. F. A. Kettle, *J. Chem. Soc.* (*A*), 1967, 314.

[10] K. Wade, *Chem. Comm.*, 1971, 792; *Inorg. Nuclear Chem. Letters*, 1972, **8**, 559.

[11] K. Wade, 'Electron Deficient Compounds,' Nelson, London, 1971.

[12] H. C. Longuett-Higgins and M. de V. Roberts, *Proc. Roy. Soc.*, 1954, *A*, **224**, 336.

[13] D. M. P. Mingos, *Nature Phys. Sci.*, 1972, **236**, 99.

[14] F. A. Cotton and T. E. Haas, *Inorg. Chem.*, 1964, **3**, 10.

[15] F. A. Cotton, 'Chemical Applications of Group Theory,' Wiley, New York, 2nd edn., 1971.

TABLE 1

Transformation properties of d, s, and p orbitals in octahedral clusters

Orbital type	Irreducible representations			
d_{z^2}, s, or p_z	A_{1g}	E_g	T_{1u}	
$d_{x^2-y^2}$	A_{2g}	E_g	T_{2u}	
d_{xy}	A_{2u}	E_u	T_{2g}	
(d_{xz}, d_{gz}), or (p_x, p_y)	T_{1g}	T_{2g}	T_{1u}	T_{2u}

one-electron molecular orbitals were obtained by solving secular equations with the form (1). The high symmetry

$$\det|H_{ij} - EG_{ij}| = 0 \qquad (1)$$

of the cobalt cluster means that the maximum dimension for these secular determinants is 5 for the molecular orbitals of T_{1u} symmetry.

For the metal symmetry adapted LCAOs we have:

$$\psi_i = \sum_\alpha a_{i\alpha}\phi_{i\alpha}$$

$$\sum a_{i\alpha}^2 = 1{\cdot}0$$

$$\int\psi_i\psi_i^*\mathrm{d}\tau = \sum_\alpha a_{i\alpha}^2 + \sum_{\alpha\neq\beta}\sum a_{i\alpha}a_{i\beta}S(i\alpha,i\beta)$$

where $S(i\alpha,i\beta) = \int\phi_{i\alpha}\phi_{i\beta}\mathrm{d}\tau$.

The LCAO–MO orbital normalised for metal–metal overlap, Φ_i, is:

$$\Phi_i = \frac{1}{(1 + X_i)^{\frac{1}{2}}}\sum_\alpha a_{i\alpha}\phi_{i\alpha}$$

$$X_i = \sum_{\alpha\neq\beta}\sum a_{i\alpha}a_{i\beta}S(i\alpha,i\beta)$$

The Coulomb integrals, H_{ii}, in equation (1) are given by:

$$\begin{aligned} H_{ii} &= \int\Phi_i\mathscr{H}\Phi_i\mathrm{d}\tau \\ &= \frac{1}{(1 + X_i)}\sum_\alpha\sum_\beta a_{i\alpha}a_{i\beta}\int\phi_{i\alpha}\mathscr{H}\phi_{i\beta}\mathrm{d}\tau \end{aligned}$$

$\int\phi_{i\alpha}\mathscr{H}\phi_{i\alpha}\mathrm{d}\tau = I_{ii}$ the valence orbital ionization energy of metal orbital i

$\int\phi_{i\alpha}\mathscr{H}\phi_{i\beta}\mathrm{d}\tau = kS(i\alpha,i\beta)I_{ii}$, according to a Wolfsberg–Helmholtz type approximation [16]

$$\int\phi_{i\alpha}\mathscr{H}\phi_{j\beta} = kS(i\alpha,j\beta)(I_{ii} + I_{jj})/2{\cdot}00$$

$$H_{ii} = \frac{(1 + kX_i)}{(1 + X_i)}I_{ii}$$

The group overlap integrals [9] G_{ij} are given by

$$\begin{aligned} G_{ij} &= \int\Phi_i\Phi_j\mathrm{d}\tau \\ &= \frac{1}{(1 + X_i)^{\frac{1}{2}}(1 + X_j)^{\frac{1}{2}}}\sum_\alpha\sum_\gamma a_{i\alpha}a_{j\gamma}S(i\alpha,j\gamma) \end{aligned}$$

and the resonance integrals H_{ij} by

$$\begin{aligned} H_{ij} &= \int\Phi_i\mathscr{H}\Phi_j\mathrm{d}\tau \\ &= \frac{1}{(1 + X_i)^{\frac{1}{2}}(1 + X_j)^{\frac{1}{2}}}\sum_\alpha\sum_\gamma a_{i\alpha}a_{j\gamma}\int\phi_i\mathscr{H}\phi_j\mathrm{d}\tau \\ &= \frac{k}{(1 + X_i)^{\frac{1}{2}}(1 + X_j)^{\frac{1}{2}}}\left\{\sum_\alpha\sum_\gamma a_{i\alpha}a_{j\gamma}S(i\alpha,j\gamma)\right\}\frac{(I_{ii} + I_{jj})}{2{\cdot}000} \\ &= \frac{kG_{ij}(I_{ii} + I_{jj})}{2{\cdot}000} \text{ (ref. 17)} \end{aligned}$$

The Coulomb integrals, H_{ii}, for the cobalt cluster are given in Table 2 in terms of overlap integrals between nearest (S_{12}) and next-nearest neighbours (S_{14}). Each of these overlap integrals has σ, π, and δ components and these are given in Table 3. It should be noted that some algebraic expressions published previously for the overlap components in octahedral clusters are in error.[14]

TABLE 2

Coulomb integrals, H_{ii}, in units of the valence orbital ionisation energies

Atomic orbital type	Symmetry of MO	H_{ii}
d_{z^2}, $d_{x^2-y^2}$, s, p_z	A	$(1 + 4kS_{12} + kS_{14})/(1 + 4S_{12} + S_{14})$
	E	$(1 - 2kS_{12} + kS_{14})/(1 - 2S_{12} + S_{14})$
	T	$(1 - kS_{14})/(1 - S_{14})$
(d_{xz}, d_{yz})	T_{1g}	$(1 + 2kS_{12} - kS_{14})/(1 + 2S_{12} - S_{14})$
	T_{2g}	$(1 - 2kS_{12} - kS_{14})/(1 - 2S_{12} - S_{14})$
(p_x, p_y)	T_{1u}	$(1 - 2kS_{12} + kS_{14})/(1 - 2S_{12} + S_{14})$
	T_{2u}	$(1 + 2kS_{12} + kS_{14})/(1 + 2S_{12} + S_{14})$
d_{xy}	A_{2u}	$(1 + 4kS_{12} - kS_{14})/(1 + 4S_{12} - S_{14})$
	E_u	$(1 - 2kS_{12} - kS_{14})/(1 - 2S_{12} - S_{14})$
	T_{2g}	$(1 + kS_{14})/(1 + S_{14})$

TABLE 3

Required overlap integrals for octahedral clusters as sums of tabulated overlap integrals [a]

$$\begin{aligned} S_{12}(d_{z^2}, d_{z^2}) &= +\tfrac{3}{16}S(d\delta, d\delta) + \tfrac{3}{4}S(d\pi, d\pi) + \tfrac{1}{16}S(d\sigma, d\sigma) \\ S_{14}(d_{z^2}, d_{z^2}) &= S(d\sigma, d\sigma) \\ S_{12}(d_{x^2-y^2}, d_{x^2-y^2}) &= -\tfrac{9}{16}S(d\delta, d\delta) - \tfrac{1}{4}S(d\pi, d\pi) - \tfrac{3}{16}S(d\sigma, d\sigma) \\ S_{14}(d_{x^2-y^2}, d_{x^2-y^2}) &= S(d\delta, d\delta) \\ S_{12}(d_{xy}, d_{xy}) &= \tfrac{1}{2}S(d\pi, d\pi) + \tfrac{1}{2}S(d\delta, d\delta) \\ S_{14}(d_{xy}, d_{xy}) &= S(d\delta, d\delta) \\ S_{12}(d_{xz}, d_{yz}) &= -\tfrac{1}{4}S(d\delta, d\delta) - \tfrac{3}{4}S(d\sigma, d\sigma) \quad (T_{1g}, T_{2g}) \\ S_{12}(d_{xz}, d_{yz}) &= -\tfrac{1}{2}S(d\pi, d\pi) - \tfrac{1}{2}S(d\delta, d\delta) \quad (T_{1u}, T_{2u}) \\ S_{14}(d_{yz}, d_{xz}) &= S(d\pi, d\pi) \\ S_{12}(s, s) &= S(s, s) \\ S_{14}(s, s) &= S(s, s) \\ S_{12}(p_z, p_z) &= \tfrac{1}{2}S(p\sigma, p\sigma) + \tfrac{1}{2}S(p\pi, p\pi) \\ S_{14}(p_z, p_z) &= S(p\sigma, p\sigma) \\ S_{12}(p_x, p_y) &= -\tfrac{1}{2}S(p\sigma, p\sigma) - \tfrac{1}{2}S(p\pi, p\pi) \quad (T_{1g}, T_{2g}) \\ S_{12}(p_y, p_x) &= -S(p_\pi, p_\pi) \quad (T_{1u}, T_{2u}) \\ S_{14}(p_x, p_y) &= S(p\pi, p\pi) \end{aligned}$$

[a] It is implicit that all tabulated overlaps are taken at appropriate values of the internuclear distance.

The components of the overlap integrals were calculated using the cobalt $3d$, $4s$, and $4p$ wave functions suggested by Richardson, Powell, Nieuwport, and Edgell [18,19] and some typical values are given in Table 4. For these calculations the cobalt–cobalt octahedral edge lengths were set equal to 0·2500 nm.[5,6,20] The charge on the cobalt atoms in such a carbonyl cluster compound must be close to zero and therefore the metal valence-orbital ionisation energies tabulated by Ballhausen and Gray have been used.[17] The eigenvectors and eigenvalues for the secular equations were solved by

---

[16] M. Wolfsberg and L. Helmholtz, *J. Chem. Phys.*, 1952, **20**, 837.

[17] H. B. Gray and C. J. Ballhausen, 'Molecular Orbital Theory,' Benjamin, New York, 1965.

[18] J. W. Richardson, R. R. Powell, and W. C. Nieuwport, *J. Chem. Phys.*, 1963, **38**, 796.

[19] J. W. Richardson, W. C. Nieuwport, R. R. Powell, and W. F. Edgell, *J. Chem. Phys.*, 1962, **36**, 1057.

[20] V. Albano, P. Chini, and V. Scatturin, *Chem. Comm.*, 1968, 163.

use of computer programmes written for the ICL 1900 computer at this College. The calculations were performed for different values of the Wolfsberg–Helmholtz constant k. The energies of the bonding and weakly antibonding molecular orbitals were rather insensitive to these changes, but the strongly antibonding molecular orbitals ($E > 0$ in Table 5) became considerably more antibonding for larger values of k.

TABLE 4

Some of the calculated overlap integrals for Co–Co = 2·50 Å

$S(d\sigma, d\sigma) = 0{\cdot}06147$

$S(d\pi, d\pi) = 0{\cdot}04804$

$S(d\delta, d\delta) = 0{\cdot}00955$

$S(s, s) = 0{\cdot}42067$

$S(p\sigma, p\sigma) = 0{\cdot}22783$

$S(p\pi, p\pi) = 0{\cdot}46155$

TABLE 5

Molecular orbital energies for the octahedral cluster Co_6 and a qualitative scheme for $Co_6(CO)_{14}{}^{4-}$

5a The isolated Co_6 cluster		5b The $Co_6(CO)_{14}{}^{4-}$ anion		
Orbital type	Energy [a]	Cluster orbital type	Metal–ligand orbital type	Comment
$E_g(4)$	3·3579	$E_g(4)$		Antibonding cluster MO's
$T_{1u}(5)$	2·1404	$T_{1u}(5)$		
$T_{1g}(2)$	1·8640	$T_{1g}(2)$		
$T_{2u}(3)$	0·1614	$T_{2u}(3)$		
$T_{1u}(4)$	−0·2241		$A_{1g}(3)^*$, $T_{1u}(4)^*$, $E_g(3)^*$ $A_{1g}(1)^*$, $T_{2g}(3)^*$, A_{2u}^*, $T_{1u}(3)^*$	Antibonding metal–ligand MO's [b]
$A_{1g}(3)$	−0·3163			
$E_g(3)$	−0·5065			
$T_{2g}(3)$	−0·4609			
$T_{1u}(3)$	−0·7271			
A_{2g}	−0·9356	A_{2g}		Bonding and weakly antibonding cluster MO's
$T_{1g}(1)$	−0·9430	$T_{1g}(1)$		
$T_{2u}(2)$	−0·9530	$T_{2u}(2)$		
$E_g(2)$	−0·9565	$E_g(2)$		
E_u	−0·9691	E_u		
$T_{2g}(2)$	−0·9874	$T_{2g}(2)$		
$T_{1u}(2)$	−0·9908	$T_{1u}(2)$		
$T_{2u}(1)$	−1·0167	$T_{2u}(1)$		
$E_g(1)$	−1·0344	$E_g(1)$		
$T_{1u}(1)$	−1·0411	$T_{1u}(1)$		
A_{2u}	−1·0510			
$A_{1g}(2)$	−1·0439	$A_{1g}(2)$		
$T_{2g}(1)$	−1·0523	$T_{2g}(1)$		
$A_{1g}(1)$	−1·0857			
			$A_{1g}(3)$, $T_{1u}(4)$, $E_g(3)$ $A_{1g}(1)$, $T_{2g}(1)$, A_{2u}, $T_{1u}(3)$	Bonding metal–ligand MO's [c]

[a] The energies are given in units of the metal d-valence orbital ionisation energy, *i.e.*, 1·000 ≡ 9·422 eV ≡ 76,000 cm^{-1}. [b] The metal–ligand antibonding molecular orbitals have the following general form: $A_{1g}(3)^* = aA_{1g}(3)$ cluster $-$ bA_{1g} carbonyl lone pairs. [c] The metal–ligand bonding molecular orbitals have the form: $A_{1g}(3) = bA_{1g}(3)$ cluster $+$ aA_{1g} carbonyl lone pairs.

RESULTS AND DISCUSSION

Table 5 gives the molecular orbital energies which resulted from the calculations for the Co_6 octahedron for the case when the Wolfsberg–Helmholtz constant $k = 1{\cdot}50$. The isolated metal cluster has 31 bonding or weakly antibonding molecular orbitals ($E < -0{\cdot}8000$) and 23 more strongly antibonding molecular orbitals ($E > -0{\cdot}8000$). Clearly the carbonyl ligands must reduce the antibonding character of some of these orbitals in order to accommodate 43 valence electron pairs in bonding or non-bonding orbitals. For the highly symmetrical $Co_6(CO)_{14}{}^{4-}$ anion (Figure 1) the the influence of the ligands on the metal orbitals can be evaluated if certain approximations are made.

For terminal carbonyl ligands the synergic bonding model is now well established and will serve as a basis for this discussion.[21] This model suggests that the overlap of the carbon sp-hybrid orbital and a metal orbital with identical symmetry characteristics results in the transfer of electron density from the carbonyl to the metal. The carbonyl π and π^* orbitals also have the correct radial characteristics to overlap with metal orbitals. Three types of orbital result: (*a*) a weakly stabilised orbital which is predominantly π(CO) and localised mainly on the oxygen atom, (*b*) an orbital localised mainly on the metal and which is stabilised owing to overlap with π^*(CO), and (*c*) a destabilised orbital derived mainly from π^*(CO) which is antibonding between metal and carbon and carbon and oxygen. Invariably (*a*)- and (*b*)-type orbitals are occupied and orbitals of type (*c*) are empty.[21] Of these π-interactions (*b*) is the most important and forms the basis of the back-donation component of the synergic mechanism.

Braterman has presented detailed arguments to show that bridging carbonyl ligands adopt a closely related bonding model.[21] For carbonyl ligands which bridge three metal atoms, a situation encountered in $Co_6(CO)_{14}{}^{4-}$, the major bonding components are (*a*) a stable bonding molecular orbital due to overlap of the carbonyl lone-pair orbital and a suitable combination of metal orbitals, and (*b*) stabilisation of those filled metal d-orbitals which have the correct symmetry characteristics to overlap with the empty π^*(CO) orbitals. Of course (*a*) and (*b*) correspond very closely to the forward- and back-donation components of the synergic mechanism used to describe terminal carbonyls. This bonding model for bridging carbonyls is illustrated in Figure 3.

For our problem the following approach will be adopted. The molecular orbitals resulting from the interactions between the carbonyl lone-pair orbitals and the metal orbitals will be evaluated initially and the effects of back donation between filled metal cluster orbitals and the π^*(CO) orbitals will then be considered.

In $Co_6(CO)_{14}{}^{4-}$ the bridging and terminal carbonyl lone-pair orbitals span the irreducible representations (2) and (3). There is only one cluster MO and one

$$\text{Terminal CO's} \quad a_{1g} \quad e_g \quad t_{1u} \qquad (2)$$

$$\text{Bridging CO's} \quad a_{1g} \quad a_{2u} \quad t_{1u} \quad t_{2g} \qquad (3)$$

ligand MO of a a_{2u} symmetry and therefore these orbitals are uniquely matched but the other ligand MO's can interact with several cluster MO's with the correct symmetry (see Table 5a). If the radial characteristics of the cluster MO's are inspected the orbital which interacts most strongly with the ligands can be evaluated with some certainty. It should also be borne in mind that overlap considerations favour the formation of cluster–ligand bonding molecular orbitals with a large

---

[21] P. S. Braterman, *Structure and Bonding*, 1972, **10**, 57.

proportion of metal 4*s* and 4*p* character.[21] Figures 4(a)—4(c) show that the terminal ligands will overlap most strongly with $A_{1g}(3)$, $E_g(3)$, and $T_{1u}(4)$ and six bonding and six antibonding molecular orbitals with these symmetries will result. The former will be localised mainly on the metal. As the bridging ligands lie on the faces of the octahedron of metal atoms $A_{1g}(1)$ and $T_{1u}(3)$ are clearly very suitable for metal–ligand bond formation [see Figures 4(a)—4(c)]. Choosing the cluster orbital most suitable for combining with the T_{2g} ligand orbitals is more problematical because $T_{2g}(1)$ has the correct radial characteristics but $T_{2g}(3)$ has more *p*-orbital character [see Figure 4(d)]. This is resolved by assuming that the bonding metal–carbonyl MO, which is localised largely on the carbonyl, has some $T_{2g}(1)$ character and the antibonding metal–ligand MO which is localised on the metal has mainly $T_{2g}(3)$ character. By this scheme $T_{2g}(1)$ remains a weakly antibonding cluster and metal–ligand MO.

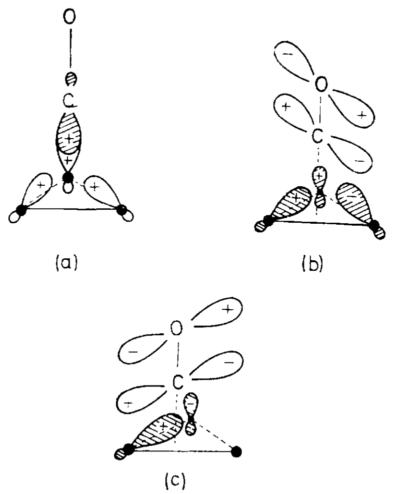
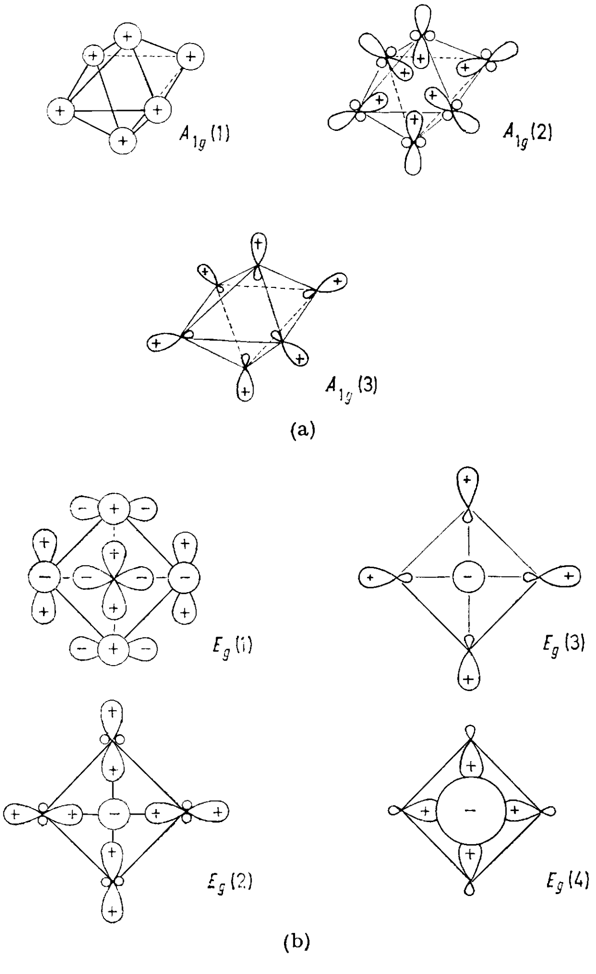


FIGURE 3 Diagrammatic representation of the bonding of a triply bridged carbonyl ligand. Local symmetry is C_{3v} and the molecular orbitals have been classified according to the irreducible representations of this point-group. (a) Illustrates forward donation from the carbonyl lone pair orbital and (b) and (c) back donation to the π^*(CO) orbitals



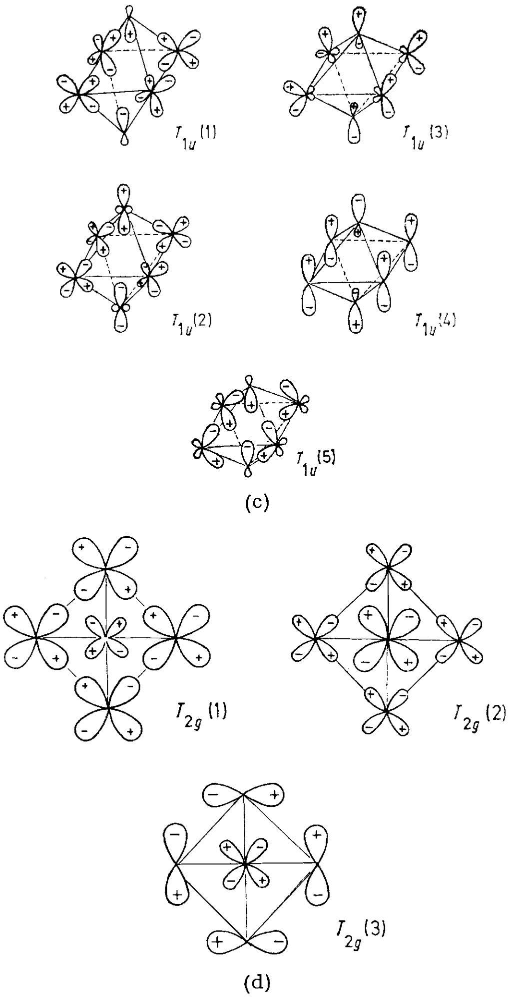


FIGURE 4 Diagrammatic representations of the molecular orbitals with A_{1g} [Figure (4a)], E_g [Figure 4(b)], T_{1u} [Figure (4c)], and T_{2g} [Figure (4d)] symmetries. The figures for E_g and T_{2g} are views down the octahedral four-fold axis

The cluster molecular orbitals for $Co_6(CO)_{14}{}^{4-}$ which result from a consideration of the σ interactions are represented schematically in Table 5b. The 86 valence electrons originating from the metal and lone pairs of the carbonyl ligands are accommodated in the 14 metal–carbon

σ-molecular orbitals and the 29 bonding and very weakly antibonding cluster molecular orbitals giving the closed-shell electronic configuration . . .$[T_{2u}(2)]^6[T_{1g}(1)]^6[A_{2g}]^2$.

The π^*(CO) orbitals of the bridging and terminal carbonyl ligands span the irreducible representations (4) and (5). Consequently the filled cluster molecular orbitals

$$\text{Terminal } \pi^*(\text{CO}) \quad t_{1g} \quad t_{2g} \quad t_{1u} \quad t_{2u} \qquad (4)$$

$$\text{Bridging } \pi^*(\text{CO}) \quad t_{1g} \quad t_{2g} \quad t_{1u} \quad t_{2u} \quad e_g \quad e_u \qquad (5)$$

belonging to these irreducible representations will be stabilised by interactions with these ligand orbitals. Nevertheless the highest occupied cluster molecular orbital, A_{2g}, is unaffected by these π-type interactions and the ground-state electronic configuration for the cluster remains . . . . . $(A_{2g})^2$.

Clearly octahedral metal carbonyl cluster compounds with more than 86 valence electrons are not likely to be formed because the additional electrons would have to occupy either antibonding cluster molecular orbitals about 80,000 cm^{-1} above the ground state or possibly antibonding metal–ligand MO's. At first glance one might suggest that $Co_6(CO)_{14}{}^{2-}$ with the electronic configuration . . . . $[T_{2u}(2)]^6[T_{2g}(1)]^6[A_{2g}]^0$ might also represent a stable diamagnetic electronic configuration for an octahedral cluster, but these calculations indicate that this hypothetical ion would have low-lying excited states. The presence of these excited states would facilitate the distortion of the octahedral molecule through vibrational modes with low force constants,[22] and an alternative cluster geometry would result. $Os_6(CO)_{18}$ which has 84 valence electrons is indeed found to have a very different geometry based on a bicapped tetrahedron of metal atoms.[23]

Wade's suggestion[10,11] that the B–H and $M(CO)_n$ fragments each contribute three hybrid orbitals for forming seven stable skeletal molecular orbitals is not strictly correct because it is not possible to define a set of MO's exclusively involved in strong skeletal bonding. In fact Wade's analogy is better expressed in terms of the number and symmetries of the antibonding MO's. Both $B_6H_6{}^{2-}$ and $Co_6(CO)_{14}{}^{4-}$ have 11 antibonding MO's with the same symmetries, *i.e.*, T_{1u}, T_{2u}, T_{1g}, and E_g. The metal orbitals with these symmetries have a very large proportion of *s* and *p* character and are very strongly antibonding because the 4*s*–4*s* and 4*p*–4*p* overlap integrals are rather large (see Table 4). In addition these MO's will be essentially unaffected by metal–ligand bond formation. Therefore the very useful analogy between boranes and transition-metal clusters result because the B–H and $M(CO)_n$ fragments each contribute three *s*–*p* hybrids for forming 11 strongly antibonding skeletal MO's. Fortunately previous papers dealing with electron counting in transition-metal clusters[10,13] still remain valid because for electron counting purposes 7 strongly bonding MO's or 11 strongly antibonding MO's which result from 18 metal hybrid orbitals are indistinguishable.

It is worth noting that the Inert Gas Rule would have been obeyed in such carbonyl clusters if there were 12 rather than 11 antibonding skeletal molecular orbitals; one for each of the edges of the octahedron. In less symmetrical octahedral carbonyl cluster compounds it is more difficult to assign the metal–ligand orbitals with the same precision but qualitatively it can be appreciated that such molecules will have a closed shell of 86 valence electrons if the ligands do not affect the 11 strongly antibonding cluster MO's substantially but interact strongly with the less antibonding $(-0{\cdot}8000 < E < 0{\cdot}0000)$ cluster MO's. This is likely to happen because only the latter have the correct radial characteristics [see Figures 4(a)—4(d)] and the strongly antibonding skeletal MO's are very unsuitable for metal–ligand bond formation.

[3/123 *Received*, 19*th January*, 1973]

---

[22] R. G. Pearson, *J. Amer. Chem. Soc.*, 1969, **91**, 4947.

[23] R. Mason, K. M. Thomas, and D. M. P. Mingos, *J. Amer. Chem. Soc.*, 1973, **95**, 3802.