solution, suggests that broadening due to the paramagnetic Ti(III) and V(III) ions exercises a complete blanketing effect.

In addition to the contents of this paper, complexes of the type $MX_4 \cdot [(CH_3)_2SiNH)]_3$, $MX_3 \cdot [(CH_3)_2SiNH]_4$, and $MX_4 \cdot [(CH_3)_2SiNH]_4$ (where M = Ti and Zr and X = Cl and Br) have also been isolated and these will be treated in full detail in a later communication.

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A Semiempirical Molecular Orbital Model for $Cr(CO)_6$, $Fe(CO)_5$, and $Ni(CO)_4$[1]

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Abstract: Molecular orbital calculations have been carried out for $Cr(CO)_6$, $Fe(CO)_5$, and $Ni(CO)_4$. The diagonal matrix elements are corrected for the effects of surrounding charges as well as for the one-center charge. The calculations are iterative and were carried out to self-consistency in the charges on all atoms, and in the configuration on the metal. The bonding in the carbonyls is discussed in terms of the Mulliken population analysis. On the basis of overlap populations it is concluded that (1) chromium 4p orbitals are involved almost entirely in the σ bonding and may be neglected in considering the π system, (2) nickel 4p orbitals are more important than 3d orbitals in π bonding to CO, (3) the π bonding in $Fe(CO)_5$ is about equally 4p and 3d in character, and (4) there is no significant difference in the bonding of the axial and equatorial CO groups in $Fe(CO)_5$. The results of the molecular calculations are compared with a variety of experimental data for the three carbonyls.

The geometrical structures of the simple transition metal carbonyl compounds $Cr(CO)_6$, $Fe(CO)_5$, and $Ni(CO)_4$ are well established. To some extent, qualitative bonding considerations appear to provide a satisfactory rationale for the stability of the metal–carbon bond in these compounds. Many questions regarding ground-state electron distributions in the three compounds are, however, not clear at this time. Variation in the metal–carbon overlap population, relative importance of 3d orbital participation, and relative importance of σ and π bonds are among the more interesting and significant aspects of the bonding. Questions related to these aspects might be clarified by a systematic treatment of the molecules at the level of a reasonably complete molecular orbital model. We report here the results of molecular orbital calculation for $Cr(CO)_6$, $Fe(CO)_5$, and $Ni(CO)_4$ in terms of a semiempirical molecular orbital model in which a number of refinements over the simplest extended Hückel model have been incorporated.

Method and Matrix Elements of the Secular Determinant

The molecular orbitals (MO's) ϕ_j are constructed from an atomic orbital basis set χ in the usual LCAO approximation.

$$\phi_j = \sum_i c_i \chi_i \tag{1}$$

Application of the variation principle leads to the familiar secular equation and determinant

$$[F - ES]C = 0 \tag{2}$$

$$|F - ES| = 0 \tag{3}$$

where F and S are the Hamiltonian and overlap matrices, respectively.

Fenske, Caulton, Radtke, and Sweeney,[2] following Richardson's separated Hamiltonian procedure, have shown that for a molecule or ion consisting of a metal atom surrounded by some number n of ligands, the diagonal matrix elements for the metal and ligands, F_{ii}^{M} and F_{ii}^{L}, respectively, can be written as

$$F_{ii}^{M} = \epsilon_i^{M}(Q_M) + CF_L(Q_L) \tag{4}$$

$$F_{ii}^{L_0} = \epsilon_i^{L_0}(Q_{L_0}) + CF_M(Q_M) + \sum_{\mu \neq 0} CF_{L\mu}(Q_{L\mu}) \tag{5}$$

$\epsilon_i(Q)$ is the orbital energy of an electron on the free atom (ion) of charge Q. $CF_L(Q_L)$ is the potential due to charge distributions on atoms surrounding the central metal. The spherical part of this potential is most important in locating the energies of the orbitals at the metal relative to those on the ligands. Analogous electrostatic potential corrections, CF_M and CF_L, are applied to the energies of orbitals centered on ligand atoms.

We assume that this charge-distribution correction can be approximated as a classical charge interaction between spherically symmetric nonoverlapping charge distributions, modified by a factor β which corrects for interpenetration of electronic charge distributions. This leads to a general expression of the form

$$F_{ii}^{T} = \epsilon_i^{T}(Q_T) - \sum_{k \neq T}^{n} \beta_{Tk} \frac{e^2 Q_k}{r_{Tk}} \tag{6}$$

The second term on the right, without a correction factor, has been employed by others in semiempirical calculations. Jørgensen refers to it as a Madelung

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[1] This research was supported by a grant from the National Science Foundation.

[2] R. F. Fenske, K. G. Caulton, D. D. Radtke, and C. C. Sweeney, *Inorg. Chem.*, **5**, 951 (1966).

correction.[3] In relation to the SCF Hamiltonian, with application of the Mulliken approximations, the term amounts to a composite of nuclear–electron and electron–electron potential terms.

Each of these potential forms exhibits a different $1/r$ dependence for r in the range of covalent bond distances or smaller. For large values for r, on the other hand, both potentials exhibit a simple $1/r$ Coulomb's law behavior. The electron–electron contribution to the Madelung term is the principal source of deviation from simple $1/r$ dependence. The following approximation, which *resembles* the Wolfsberg–Helmholtz formula, is used for the off-diagonal Hamiltonian matrix elements

$$F_{ij} = \frac{S_{ij}}{2}(\epsilon_i + \epsilon_j)\kappa \qquad (7)$$

ϵ_i and ϵ_j represent the orbital energies of the ith and jth orbitals, *corrected for the charge on those centers; i.e.*, they represent the first term on the right in eq 6.

The omission of the Madelung corrections from eq 7 cannot be rigorously justified, since the Wolfsberg–Helmholtz approximation is itself empirical. There is, however, no obvious connection between the Madelung correction and terms which have been dropped from a more complete expression for F_{ij}. In an empirical sense, the Madelung terms should not be included, since they lead to unreasonable values for F_{ij}, especially when highly polar species are involved. We have chosen to employ a single value for κ, 1.75, for all off-diagonal matrix elements. This seems preferable to adding still more empirical parameters to the model, since there is not yet a general basis on which to classify the off-diagonal elements with respect to appropriate values for κ.

Basis Sets, Atomic Orbitals, Population Analysis, and Self-Consistency Criterion. The geometries employed in this work are those reported in references 4, 5, and 6 for $Ni(CO)_4$, $Fe(CO)_5$, and $Cr(CO)_6$, respectively. Some controversy still appears to exist concerning small differences in axial and radial interatomic distances[5,7] in Fe–C–O linkages, but such small differences would not affect our final conclusions.

The basis for the transition metal carbonyls consisted of 2s and 2p functions for carbon and oxygen atoms and 3d, 4s, and 4p functions of the neutral metal atom.

The radial parameters of all 2s and 2p functions were obtained from Clementi and Raimondi,[8] used without modification. For the purpose of subsequent calculation of transition moments and to economize computer time, it was desirable to employ single exponential functions also for the transition-metal orbitals. Since $Cr(CO)_6$, $Fe(CO)_5$, and $Ni(CO)_4$ form a closely related series of molecules in the first transition row, the complete overlap matrix of the intermediate member, $Fe(CO)_5$, was computed using Clementi's many-term SCF iron 3d and 4s functions;[9] 4p functions were taken from Richardson, *et al.*[10]

Elements of the overlap matrix derived from these complex functions were compared to those obtained using several single exponent Slater-type orbital functions. For the 4s orbital on iron, the Clementi–Raimondi function[8] gave good agreement with the SCF function result. The Clementi–Raimondi exponent values were accordingly used for the 4s orbitals of chromium and nickel. Similarly, Burns[11] exponents for the 4p functions appeared most satisfactory, and Burns' values for the chromium and nickel 4p orbital exponents were employed. For the 3d functions, it was necessary to interpolate between Burns and Slater values. Chromium and nickel functions were thus determined from conclusions based on the analysis of overlaps in the case of $Fe(CO)_5$.

Total orbital populations, p_j, gross electron population at atom A, P_A, net atomic charge at atom A, Q_A, overlap populations between atoms A and B, P_{AB}, and between orbitals i and j, P_{ij}, were computed conventionally as follows[12]

$$p_j = \sum_k^{\text{occ}} N_k c_{jk}^2 + \sum_k^{\text{occ}} \sum_{i \neq j} N_k c_{ik} c_{jk} S_{ij} \qquad (8)$$

$$P_A = \sum_k^{\text{occ}} \sum_i^{A} N_k c_{ik}^2 + \sum_k^{\text{occ}} \sum_i^{A} \sum_{j \neq i} N_k c_{ik} c_{jk} S_{ij} \qquad (9)$$

$$Q_A = Z_A - P_A \qquad (10)$$

$$P_{AB} = 2 \sum_k^{\text{occ}} \sum_i^{A} \sum_{j \neq i}^{B} N_k c_{ik} c_{jk} S_{ij} \qquad (11)$$

$$P_{ij} = 2 \sum_k^{\text{occ}} N_k c_{ik} c_{jk} S_{ij} \qquad (12)$$

Z_A is the core charge of atom A (nuclear charge minus the number of core electrons of the neutral atom). Information about the gth MO can be obtained by summing eq 8, 9, 11, and 12 only over $k = g$.

To facilitate an analysis of the population elements described above in terms of σ and π bonding, carbon orbitals were orthogonally transformed where necessary from a completely collinear molecular coordinate system to one in which the coordinate system at carbon is oriented toward the metal atom.

Molecular orbitals derived from solution of the secular equation are dependent on the charges assumed for the atoms and the configuration assumed for the transition metal. Accordingly, it was necessary to employ an iterative procedure in which the charges on atoms and the metal configuration were varied to achieve self-consistency. In the present method one proceeds by assuming a set of atomic charges $Q_k^{(1)}$ based on chemical intuition. Next, the quantities given by equations which define F_{ii}, F_{ij}, and S_{ij} are calculated. The solutions of eq 2 and 3 result in a set of molecular orbitals, coefficients of which make up matrix C. With C and S, one computes gross electron populations P_A, orbital populations p_j, and the set of atomic charges, $Q_k^{(2)}$ (*vide supra*).

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The convergence criterion is that iterative cycles $f - 1$ and f produce conditions

$$|Q_k^{(f-1)} - Q_k^{f}| \leqslant \delta_Q \qquad (13)$$

$$|\sigma_j^{(f-1)} - \sigma^{f}| \leqslant \delta_Q \qquad (14)$$

for all atoms and metal orbital populations, respectively. σ_j indicates the total population of an orbital type j on a given center

$$\sigma_j = \sum_n p_n \qquad (15)$$

where Σ is taken over all orbitals of that type (*e.g.*, the five 3d orbitals on the metal) and $\delta_Q = 0.01\text{–}0.05$. For the typical cycling step, both input Q and σ for the $(i + 1)$th cycle are weighted averages

$$Q_k^{(i+1)} = wQ_k^{(i_{\text{in}})} + zQ_k^{(i_{\text{out}})} \qquad (16)$$

$$\sigma_j^{(i+1)} = w\sigma_j^{(i_{\text{in}})} + z\sigma_j^{(i_{\text{out}})} \qquad (17)$$

where $w + z = 1$, and usually $0.8 \leq w \leq 0.93$. The smallness of z assures reasonably damped iterative charge oscillations. Between 5 and 15 cycles of iteration are often required to achieve convergence. This procedure resembles the SCCC method in part.[13]

Evaluation of Terms in Matrix Elements *F* and other Quantities.

Orbital energy ϵ^{T} is the first term in eq 6. It was obtained in one of two ways, depending on whether T is a metal (ϵ^{M}) or nonmetal center (ϵ^{L}). For metal orbitals (3d, 4s, 4p), ϵ was obtained by taking linear combinations of valence orbital ionization potentials (VOIP's), *viz.*

$$\epsilon_i^{\text{M}} = -\sum_k b_k(\text{VOIP})_k \qquad (18)$$

$$(\text{VOIP})_k = A_kQ_{\text{M}}^2 + B_kQ_{\text{M}} + C_k \qquad (19)$$

k is the configuration (*e.g.*, $3d^94s^1$ for Ni^0). The advantages of using VOIP's and additional details regarding their use are described elsewhere.[14] The orbital energies for nonmetals are derived from

$$\epsilon_j^{\text{L}} = -(\text{VSIE})_{\text{L}j}\,(Q = 0) - K_{\text{L}}Q_{\text{L}} \qquad (20)$$

for the jth AO on atom L, which has a charge-sensitivity parameter K_{L} (eV per unit positive charge). Average zero-charge VSIE's determined from Cusachs and Reynolds' smoothed values were used, and K_{L}'s were obtained from the same source.[15] It should be emphasized that these K are based on atomic data and are not arbitrarily chosen parameters.

Experience gained from calculations on diatomic molecules[16] indicates that β of eq 6 is usually on the order of 0.8–0.9. In the calculations on Cr(CO)_6, Fe(CO)_5, and Ni(CO)_4, the numerical values of the penetration parameters for the M–C interactions were based on an overlap integral quantity; *viz.*, relative β (eq 6) were chosen to depend on relative overlaps

$$\beta = 1 - 0.14S(\text{M–C})/S(\text{Ni–C}) \qquad (21)$$

S(M–C) is the total overlap between metal d orbitals and carbon orbitals. The constant -0.14 was chosen empirically in the light of experience gained in calculations on diatomic molecules, and to provide a slightly negative charge on nickel, as obtained by Nieuwpoort.[17] This constant is thus simply scaled for the other two carbonyls by assuming that the correction constant should increase linearly with increase in metal–carbon overlaps. The resulting final values of β for the three M–C interactions were thus Cr–C = 0.78, Fe–C = 0.80, Ni–C = 0.86. In the two-center terms involving carbon and oxygen atoms 0.70 was used for β_{CO}. The classical point-charge approximation was employed without a penetration correction in evaluating interactions between nonbonded centers. The sensitivity of the final energy level ordering and ground-state electron distribution to the values chosen for β was examined in the case of Ni(CO)_4. A value for β of $+1.1$ for the M–C resulted in a final Ni charge of 0.56 but resulted in no significant change in the energy level diagram nor in over-all overlap populations, etc.

Transition moments for allowed one-electron transitions in Ni(CO)_4 and Cr(CO)_6 were quantitatively evaluated. Each component of the degenerate excited state was represented as a single determinant. Following group theoretical considerations, transition moments, $\mathbf{M}_{jk}$, and transition probabilities derived therefrom, for electronic transitions between molecular orbitals j and k were computed using the distance operator

$$\mathbf{M}_{jk} = -e\langle\phi_j|\sum_i^{\text{el}}\mathbf{r}_i|\phi_k\rangle = -eC_j^{\text{T}}\mathbf{R}C_k \qquad (22)$$

$$\mathbf{R}_{\text{mn}} = \langle\chi_{\text{m}}|\mathbf{r}|\chi_{\text{n}}\rangle \qquad (23)$$

The one-electron, two-center dipole moment matrix elements over atomic orbitals were evaluated explicitly over all centers, with the origin at the metal. Three-center integrals were obtained from

$$\langle\chi_\mu|\mathbf{r}_{\text{M}}|\chi_\nu\rangle = \langle\chi_\mu|\mathbf{r} + \mathbf{r}_{1/2}|\chi_\nu\rangle \qquad (24)$$

which derives from the sum $\mathbf{r}_{\text{M}} = \mathbf{r} + \mathbf{r}_{1/2}$. The quantity $\mathbf{r}_{1/2}$ is the moment operator centered at the midpoint between ligand centers m and n, and $\mathbf{r}$ is the metal-to-midpoint vector. Equation 24 reduces to overlap and two-center moment integrals. One-center metal components are small and were not included.[18]

Results and Discussion

A number of ground-state properties for the three metal carbonyls Ni(CO)_4, Fe(CO)_5, and Cr(CO)_6 were interpreted using the molecular wave functions derived by the present semiempirical approach.[19] The results can be compared among the three related metal carbonyls and may be compared with available experimental data for the compounds. Table I contains the converged atomic charges.

In all cases the charges at the metal are small, and the carbon and oxygen charges are also small as ex-

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[19] A tabulation of eigenvalues, eigenvectors, and overlap integrals has been deposited as Document No. 9856 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. 20540. A copy may be secured by citing the document number and by advance remittance ($2.50 for photoprints of $1.75 for 35-mm microfilm) payable to: Chief, Photoduplication Service, Library of Congress.

Table I. Net Atomic Charges in $Ni(CO)_4$, $Fe(CO)_5$, and $Cr(CO)_6$

Molecule	Metal	Carbon	Oxygen
$Ni(CO)_4$	−0.735	0.218	−0.034
$Fe(CO)_5$	0.57	0.256 (av)	−0.39 (av)
$Cr(CO)_6$	0.63	0.099	−0.204

pected. The population analysis for $Ni(CO)_4$ yields results which are close to those obtained in an SCF calculation[17] using a valence orbital basis set. The SCF value for the charge on nickel, also based on a Mulliken population analysis, is −1.0.

In what follows comparisons will be made between the three carbonyls. The self-consistent atomic orbital populations, p, are given for $Cr(CO)_6$, $Fe(CO)_5$, and $Ni(CO)_4$ in Table II. It is of interest to compare present results with those obtained by Nieuwpoort for $Ni(CO)_4$: $3d^{8.34}4s^{0.84}4p^{1.9}$. Nieuwpoort obtains a higher 4s orbital population than found here, but the over-all results are in reasonable agreement. By comparison the 4p orbital populations in $Cr(CO)_6$ and $Fe(CO)_5$ are somewhat lower than in $Ni(CO)_4$, but the 3d orbital populations are relatively higher, *i.e.*, in comparison with free-atom values.

Table II. Self-Consistent Charge Atomic Orbital Populations in $Ni(CO)_4$, $Fe(CO)_5$, and $Cr(CO)_6$

Orbital type	Atom population					
	$Ni(CO)_4$		$Fe(CO)_5$[a]		$Cr(CO)_6$	
3d	Ni	9.255	Fe	6.744	Cr	4.80
4s		0.13		0.275		0.22
4p		1.35		0.414		0.31
2s	C	1.431	C	1.346 (1.35)	C	1.38
2p		2.241		2.356 (2.405)		2.52
2s	O	1.634	O	1.708 (1.727)	O	1.18
2p		4.404		4.648 (4.71)		4.52

[a] Numbers inside and outside the parentheses refer to atomic orbitals on atoms in axial and trigonal positions, respectively.

Atom–atom overlap populations (eq 11) in the carbonyls are given in Table III. It is noteworthy that the metal–carbon population is lower in $Ni(CO)_4$ than in either $Cr(CO)_6$ or $Fe(CO)_5$; the carbon–oxygen overlap population in $Ni(CO)_4$ is, conversely, higher than in $Cr(CO)_6$ and $Fe(CO)_5$. Overlap populations in $Fe(CO)_5$ and $Cr(CO)_6$ are similar. Table IV contains a summary of the σ and π bond overlap populations in the M–C bonds of the three carbonyls. Table V lists additional details for $Cr(CO)_6$ and $Ni(CO)_4$.

Table III. Atom–Atom Overlap Populations in $Ni(CO)_4$, $Fe(CO)_5$, and $Cr(CO)_6$

Molecule	Atoms	Carbon	Oxygen
$Ni(CO)_4$	Nickel	0.3933	...
	Carbon	...	1.5894
$Fe(CO)_5$	Iron	0.4792 (av)[a]	...
	Carbon	...	1.3146 (av)[b]
$Cr(CO)_6$	Chromium	0.4626	...
	Carbon	...	1.372

[a] Fe–C axial = 0.4553; Fe–C trigonal = 0.4963. [b] C–O axial = 1.332; C–O trigonal = 1.2886.

Table IV. Metal–Carbon Overlap Populations[a]

Bond	Metal orbitals	Overlap populations σ	π
Cr–C	3d	0.4848	0.2476
	4s	0.4416	...
	4p	0.1830	0.0268
Fe–C	3d	0.3142	0.1958
	4s	0.4645	...
	4p	0.4070	0.1515
Ni–C	3d	0.0377	0.0649
	4s	0.17	...
	4p	0.350	0.1319

[a] σ and π overlap populations between all metal orbitals of one type and all carbon orbitals of the molecule.

Table V. Overlap Populations of Metal and Carbon Orbitals in M–C and C–O Bonds, Respectively, of $Cr(CO)_6$ and $Ni(CO)_4$[a]

Bond	Orbital	σ	π
Cr–C	3d (e_g)	0.4848	...
	3d (t_{2g})	...	0.2476
	4s	0.4416	...
	4p	0.1830	0.0268
C–O	$2p_\sigma$ (C)	0.4325	...
	$2p_\pi$ (C)	...	0.3025
	2s (C)	0.3329	...
Ni–C	3d (e)	...	0.0444
	3d (t_2)	0.0377	0.0205
	4s	0.17	...
	4p	0.350	0.1319
C–O	$2p_\sigma$ (C)	0.4260	...
	$2p_\pi$ (C)	...	0.3685
	2s (C)	0.4265	...

[a] In each case the total σ and π populations per metal orbital of each type are given.

It is of particular interest to note that the 4p orbitals of chromium in $Cr(CO)_6$ are employed almost exclusively in σ bonding. On the other hand, π bonding from 3d orbitals of Cr is extensive. These results substantiate the simplification frequently employed, in which the π bonding in the group VI carbonyls is viewed entirely in terms of 3d interactions with the CO ligands. In $Ni(CO)_4$ the over-all d-orbital overlap populations are much lower than in the chromium compound. On the other hand, p-orbital participation in bonding is greater; *the 4p orbitals are the major contributors to π bonding in $Ni(CO)_4$*. In $Fe(CO)_5$ the 3d and 4p orbitals are involved extensively in π bonding and to nearly the same extent. Therefore, the 3d orbitals in both $Cr(CO)_6$ and $Fe(CO)_5$ are important in net π bonding.

We summarize the conclusions regarding the relative importances of the metal orbitals in M–C bonding in the three carbonyls.

	σ bonds	π bonds
3d	Ni < Fe ≈ Cr	Ni < Fe ≈ Cr
4s	Ni < Cr < Fe	...
4p	Cr < Ni ≈ Fe	Cr < Ni ≈ Fe

In the case of $Fe(CO)_5$ the population analysis indicates that the axial carbonyls are slightly *less* strongly bonded to the metal than the radial. Since a slightly shorter axial Fe–C distance was assumed, this result occurs despite factors which might have been expected to lead to greater bonding to the axial groups. The calculations thus do not support the contention[5a] that the axial CO groups are more strongly bonded than the radial.

Relative overlap populations may be considered as measures of relative bond strengths. Therefore, upon associating relative M–CO bond strengths with mean dissociation energies, $\bar{D}$(M–CO), relative overlap populations can be associated with the latter. For the process

$$\mathrm{M(CO)}_n\mathrm{(g)} \longrightarrow \mathrm{M(g)} + n\mathrm{CO(g)} \tag{25}$$

the mean dissociation energy is defined in terms of heats of formation

$$\bar{D}(\mathrm{M{-}CO}) = \Delta H/n \tag{26}$$

and

$$\Delta H = \Delta H_f(\mathrm{M^*,g}) + n\Delta H_f(\mathrm{CO^*,g}) - \Delta H_f[\mathrm{M(CO)}_n\mathrm{,g}] \tag{27}$$

where M* and CO* refer to the product species in appropriate valence states.[20]

Table VI displays mean M–CO bond dissociation energies, weighted mean metal–carbon and carbon–oxygen stretching frequencies (*vide infra*), $\bar{\nu}$, and metal–carbon and carbon–oxygen overlap populations of the three carbonyls. There is a nearly linear relationship between computed M–C overlap population and M–CO dissociation energies.

Table VI. Mean M–CO Bond Dissociation Energies, $\bar{D}$(M–CO), Computed M–C and C–O Overlap Populations, and Mean M–C and C–O Stretching Frequencies

Compound	$\bar{\nu}_{MC}$, cm^{-1}	$\bar{D}$ (M–CO), kcal[a,b]	M–C overlap population	$\bar{\nu}_{CO}$, cm^{-1}	CO overlap population
$Ni(CO)_4$	412	77	0.3933	2075	1.589
$Cr(CO)_6$	407	87	0.4626	2028	1.372
$Fe(CO)_5$	422	89	0.4792	2038	1.332

[a] Includes the energy necessary to promote the gaseous atom from the ground state to excited state (all electrons paired in lowest unoccupied d orbitals): $(1/n)\mathrm{M(CO)}_n\mathrm{(g)} \rightarrow (1/n)\mathrm{M(g)} + \mathrm{CO(g)}$. [b] For $Ni(CO)_4$, $Cr(CO)_6$, and $Fe(CO)_5$ thermodynamic data, see F. A. Cotton, A. K. Fischer, and G. Wilkinson, *J. Am. Chem. Soc.*, **81**, 800 (1959); A. K. Fischer, F. A. Cotton, and G. Wilkinson, *ibid.*, 79, 2044 (1957); F. A. Cotton, A. K. Fischer, and G. Wilkinson, *ibid.*, **78**, 5168 (1956).

It is also desirable to determine whether there exist reasonable relationships between computed M–C and C–O overlap populations of the metal carbonyls and their M–C and C–O vibrational stretching frequencies, respectively. It has already been pointed out in several places that there exists a linear relationship between CO stretching frequencies in organic carbonyl compounds and the computed CO bond orders.[21,22] However, because of the presence of several carbonyl groups and their particular symmetry arrangements in the metal carbonyls, there exist several stretching modes, with different frequencies. It is inappropriate to compare any one of a number of possible vibrational frequencies of a molecule with a presumably corresponding frequency in another molecule, which has quite different symmetry, because the interaction force constants enter in a different way in the two cases. However, since the CO stretching frequencies of different symmetries do not differ widely in the metal carbonyls, mean values of ν_{CO}, obtained by averaging the frequencies, weighted according to the degeneracy of the normal mode, yield a characteristic frequency ($\bar{\nu}_{CO}$) which is approximately free of the influence of interaction force constants (Table VI). Similar reasoning is applicable to MC stretching frequencies, although mixing with other modes is more extensive and comparisons less valuable.

Table VII displays C–O and M–C stretching frequencies from which the weighted mean frequencies shown in Table VI were derived. Comparisons with computed overlap populations are only qualitative, especially with $Fe(CO)_5$, since the five CO groups are not all vibrationally equivalent in this compound. Variations of the metal–carbon overlap populations and wave numbers of the mean M–C vibrations do not correlate very well, as might have been expected. The distinctly higher CO stretching mode of $Ni(CO)_4$ relative to $Cr(CO)_6$ and $Fe(CO)_5$ is in accord with the expectations based on CO overlap populations. The CO overlap populations and values of $\bar{\nu}_{CO}$ for $Fe(CO)_5$ and $Cr(CO)_6$ are nearly the same.

Table VII. C–O and M–C Vibrational Frequencies of $Ni(CO)_4$, $Fe(CO)_5$, and $Cr(CO)_6$

Compound	ν_{CO}, cm^{-1}	ν_{MC}, cm^{-1}	Symmetry	Ref
$Ni(CO)_4$	2057	422	F_2	
	2128	381	A_1	*a*
$Fe(CO)_5$	2014, 2117, 1984	474, 414, 377	A_2'', A_1'	
	2034	431	E'	*b*
$Cr(CO)_6$	2000	441	F_{1u}	
	2118	390	A_{1g}	
	2026	363	E_g	*c*

[a] L. H. Jones, *J. Chem. Phys.*, **28**, 1215 (1958). [b] W. F. Edgell, W. E. Wilson, and R. Summit, *Spectrochim. Acta*, **19**, 863 (1963). [c] L. H. Jones, *ibid.*, **19**, 329 (1963).

It is possible to estimate the correctness of the presently computed chromium charge (+0.63) in $Cr(CO)_6$. From the *k*-edge absorption experiment on $Cr(CO)_6$ a charge of 0.4 was deduced for chromium.[23] It is also possible to estimate quantitatively the π-acceptor ability of ligand CO in $Cr(CO)_6$, and to obtain a better understanding of the electronic rearrangement that occurs when CO bonds to Cr in $Cr(CO)_6$. On the basis of a force-constant-bond-order analysis Cotton has suggested that CO accepts 0.5 electron pair *via* π bonding.[24] Dobson has concluded that this figure is too high and estimates that 0.22 to 0.26 of an electron pair is accepted by CO *via* π bonding.[25] The basis of Dobson's estimate is, however, also questionable.

Table VIII contains population analysis data for π atomic orbitals in free CO and for the π atomic orbitals of CO in $Cr(CO)_6$. It is evident that carbon p_π atomic orbitals contain more charge when CO is bonded to chromium. On the other hand, the p_π charge of oxygen is nearly unaffected. The total π charge accepted by one CO ligand is 0.576 electron (or 0.288

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[20] H. A. Skinner, "Advances in Organometallic Chemistry," Vol. 2, F. G. A. Stone and R. West, Ed., Academic Press Inc., New York, N. Y., 1964.

[21] S. Forsen, *Spectrochim. Acta*, **18**, 595 (1962).

[22] S. Bratož and S. Besnainou, *J. Chem. Phys.*, **34**, 1142 (1961).

[23] R. L. Barinskii and C. G. Nadzhakov, *Izv. Akad. Nauk SSSR, Ser. Fiz.*, **24**, 407 (1960).

[24] F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964).

[25] G. R. Dobson, *ibid.*, **4**, 1673 (1965).

electron pair). The π-electron acceptance for CO (0.288 electron pair) is, therefore, nearly equal to that derived from the most recent analysis of vibrational data. From a similar analysis of σ orbitals it is concluded that CO donates 0.471 electronic charge to chromium through σ bonding.

Table VIII. Populations in π-Bonding Carbon and Oxygen Orbitals in CO and $Cr(CO)_6$

	CO		$Cr(CO)_6$	
Populations	Carbon	Oxygen	Carbon	Oxygen
2 pπ AO	0.52	1.480	0.8372	1.451
π electrons	1.04	2.960	1.6744	2.902
Total π electrons	4.00		4.576	
π electrons accepted by CO in $Cr(CO)_6$			0.576 (0.288 electron pair)	

The Mössbauer isomer shift (IS) of iron compounds, and those of other select atoms, can be interpreted qualitatively in the light of computed charge and electronic configuration of the bonded metal atom. Conversely, IS can be used to gain insights into the correctness of the computed charge and configuration of the metal atom. It has been shown that IS depends on the iron 4s electron density at the nucleus and can be obtained from

$$IS = \frac{2\pi}{5}Ze^2[|\Psi_{abs}(0)|^2 - |\Psi_s(0)|^2](R_{ex}^2 - R_{gd}^2) \quad (28)$$

where Z, $|\Psi_{abs}|^2$, and $|\Psi_s|^2$ are the nuclear charge and the total s-electron densities (1s, 2s, 3s, and 4s) at the absorber and source nuclei, respectively,[26] R_{ex} and R_{gd} are the nuclear radii in nuclear excited and ground states, respectively. Since it is reasonable to assume that source and absorber have the same 1s, 2s, and 3s electron densities at the respective nuclei, IS will be nonzero only when source and absorber nuclei have unequal 4s electron densities. Since $R_{ex} < R_{gd}$, and both are constants, eq 28 can be rewritten

$$IS = w[|\Psi_s(0)|^2 - |\Psi_{abs}(0)|^2] \quad (29)$$

where $w = (2\pi/5)Ze^2(|R_{ex}^2 - R_{gd}^2|)$. Equation 29 illustrates that IS is positive whenever the s-electron density at the absorber nucleus, $|\Psi_{abs}|^2$, is less than the s-electron density at the metal source, $|\Psi_s|^2$.

Using results from Watson's Hartree–Fock calculations, Walker, Wertheim, and Jaccarino have constructed graphs relating electronic configurations of iron compounds to isomer shifts.[26] Using the presently computed 3d4s configuration, $3d^{6.7444}4s^{0.275}$, the value for the isomer shift in $Fe(CO)_5$ is estimated to be +0.09 mm/sec by interpolating between the d^6 and d^7 configuration graphs. The experimental value[27] is 0.035 ± 0.043 mm/sec, which would be predicted from the configuration $3d^{6.7444}4s^{0.675}$.

The properties of the metal carbonyls just discussed relate to molecular electronic ground states. Certain other physical properties have been found empirically to relate to the ground-state electron distribution, even though computation of the expectation values for these quantities would require application of first- or second-order perturbation theory. For example, nmr chemical shifts of several nuclei have been found to vary in the same direction as computed electronic charges at those atoms. While there are several magnetic effects to be considered in calculating nmr chemical shifts, the local paramagnetic effect has been found dominant.[28–30] This effect has an electronic charge dependence, and linear relationships between ^{13}C, ^{31}P, ^{35}Cl, and ^{19}F chemical shifts and electronic charges have been demonstrated.[31] It has been observed that replacement of directly bonded hydrogen or carbon atoms in organic carbonyls by more electronegative substituents results in a high-field shift of the ^{13}C resonance of the carbonyl carbon.[32]

Table IX lists CO overlap populations, calculated charges at oxygen and carbon, and ^{13}C and ^{17}O chemical shift data for the three transition metal carbonyls. The chemical shift values for ^{13}C do not correlate with the calculated atomic charges on carbon but do correlate very satisfactorily with the metal charges and with carbon–oxygen overlap populations. It seems likely that the Madelung correction exerts an influence on the distribution of charge betweeen C and O as the number of CO groups about the metal changes in the series, so that the calculated C or O charge variations by themselves do not entirely determine the chemical shift variation. The metal–carbonyl interactions are less geometry dependent and appear to be more reliably related to the actual charges on carbon in the series. The chemical shift values for ^{17}O in $Fe(CO)_5$ and $Ni(CO)_4$ correlate with CO overlap population and metal charges in the manner of ^{13}C shifts. The ^{17}O chemical shift of $Cr(CO)_6$ has not yet been reported.

Table IX. CO Overlap Populations, Carbon, Metal, and Oxygen Charges, and ^{13}C and ^{17}O Chemical Shifts in $Ni(CO)_4$, $Fe(CO)_5$, and $Cr(CO)_6$

	$Ni(CO)_4$	$Fe(CO)_5$	$Cr(CO)_6$
P_{CO}	1.589	1.315	1.372
Q_C	0.218	0.256	0.099
Q_O	−0.034	−0.39	−0.204
Q_M	−0.735	+0.57	+0.63
δ, ^{13}C	−64 ± 5[a]	−85 ± 1[a]	−83.1 ± 0.06[b]
δ, ^{17}O	−362[c]	−388[c]	...

[a] R. Bramley, B. N. Figgis, and R. S. Nyholm, *Trans. Faraday Soc.*, **58**, 1893 (1962); in ppm relative to internal benzene. [b] In ppm relative to external benzene; $Cr(CO)_6$ in chloroform solution. We are grateful to Dr. R. J. Pugmire and Professor D. M. Grant of the Department of Chemistry, University of Utah, for this determination. [c] In ppm relative to H_2O; see Bramley, *et al.*, footnote *a*.

The correspondence between the computed energies of the highest occupied energy levels in the three carbonyls and the observed first ionization potentials is poor (Table X). This is almost certainly a result of using the empirical Wolfsberg–Helmholtz-type approximation.

(26) L. R. Walker, G. K. Wertheim, and V. Jaccarino, *Phys. Rev. Letters*, **6**, 98 (1951).

(27) R. H. Herber, W. R. Kingston, and G. K. Wertheim, *Inorg. Chem.*, **2**, 153 (1963).

(28) J. A. Pople, *Mol. Phys.*, 7, 301 (1964); *J. Chem. Phys.*, 37, 53 (1962).

(29) A. Saika and C. P. Slichter, *ibid.*, 22, 26 (1954).

(30) H. Spieseche and W. G. Schneider, *ibid.*, 35, 722 (1961).

(31) J. M. Sichel and M. A. Whitehead, *Theoret. Chim. Acta*, **5**, 35 (1966), and references therein.

(32) J. B. Stothers and P. C. Lauterbur, *Can. J. Chem.*, **42**, 1563 (1964).

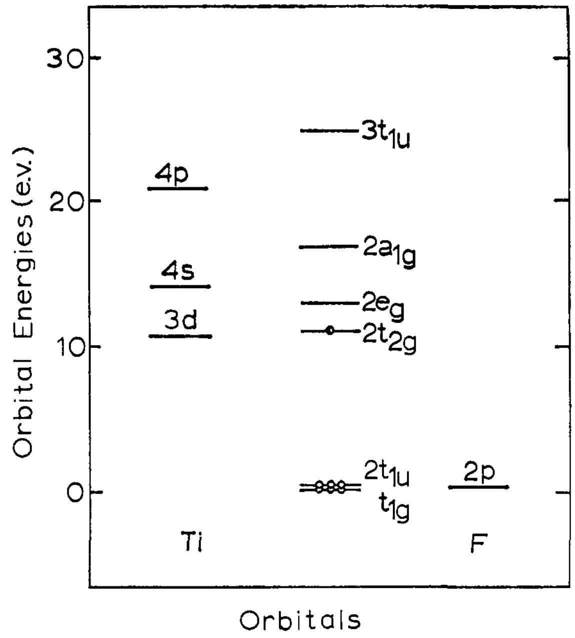

Figure 1. Partial molecular orbital energy level diagram for $[TiF_6]^{3-}$. The circles and half-circle represent electron pairs and one electron, respectively.

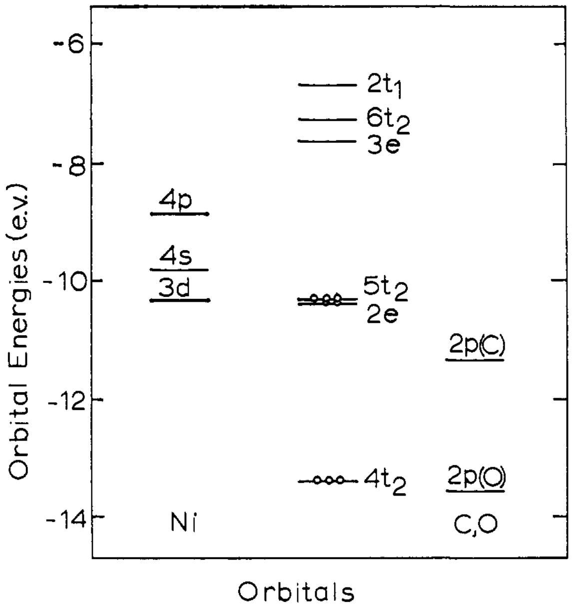

Figure 2. Partial molecular orbital energy level diagram for $Ni(CO)_4$. Circles represent electron pairs.

A quantitatively reliable assignment of absorption bands in electronic spectra requires accurate knowledge of both ground- and excited-state wave functions. Although the higher energy molecular orbitals are reproduced rather poorly in an MO calculation of the type reported here, it is worthwhile to examine the energy level diagram for at least some qualitative features of the electronic spectrum. The attempt is made here to assign the observed electronic bands on the basis of energy differences of one-electron MO's, calculated oscillator strengths, and chemical considerations. The study of the carbonyls was undertaken following a preliminary investigation of the simpler hexafluorotitanate(III) ion, $[TiF_6]^{3-}$. The calculational procedure is the same as that employed in treating the carbonyls. A partial MO energy level diagram of $[TiF_6]^{3-}$ is shown in Figure 1. $[TiF_6]^{3-}$ has a symmetry-forbidden band at 1.98 eV, which corresponds to the quantity 10*Dq* of crystal-field theory. The energy level diagram indicates that the band is due to a $2t_{2g}(\pi^b) \rightarrow 2e_g(\sigma^*)$ transition. The calculated value of 10*Dq* is 1.83 eV, in good agreement with experiment. Several other general features of the results for $[TiF_6]^{3-}$ resemble those obtained in a more elaborate calculation.[2] We find that both $2e_g$ and $2t_{2g}$ MO levels are positive; MO's with lower energy than $2t_{2g}$ are closely spaced; and $2t_{2g}$, $2e_g$, and $3t_{1u}$ levels are spaced more widely than levels below $2t_{2g}$. The computed

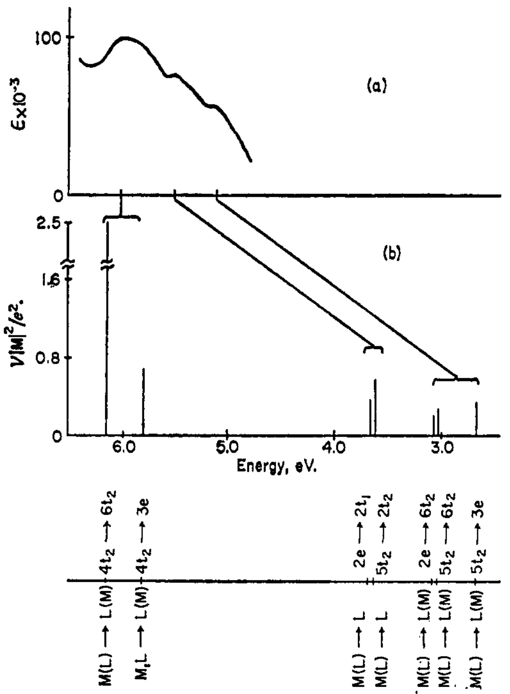

Figure 3. Experimental (a) and calculated (b) electronic spectra for $Ni(CO)_4$. Symbols M or L refer to molecular orbitals which are entirely metal or ligand, respectively, in character. M(L) or L(M) refer to orbitals which are largely metal or ligand, respectively, but which contain some of the other. M,L refers to orbitals which are admixtures of comparable metal and ligand components.

Table X. Molecular Ionization Potentials of $Ni(CO)_4$, $Fe(CO)_5$, and $Cr(CO)_6$

Compound	Ionization potential, eV Exptl[a]	Ionization potential, eV Energy of highest occupied MO
$Ni(CO)_4$	8.64 ± 0.15[b] 8.35 ± 0.15[c] (8.28)[e]	−10.37
$Fe(CO)_5$	8.53 ± 0.2[b] (7.95)[e]	−14.43
$Cr(CO)_6$	8.15 ± 0.17[d] (8.03)[e]	−12.75

[a] Mass spectrometric (photometric). [b] R. E. Winters and R. W. Kiser, *Inorg. Chem.*, **3**, 699 (1964). [c] S. M. Schildcrout, G. A. Pressley, Jr., and F. E. Stafford, *J. Am. Chem. Soc.*, **89**, 1617 (1967). [d] R. E. Winters and R. W. Kiser, *Inorg. Chem.*, **4**, 157 (1965). [e] F. I. Vileson and B. C. Kurbaton, *Dokl. Akad. Nauk SSSR*, **140**, 1364 (1961).

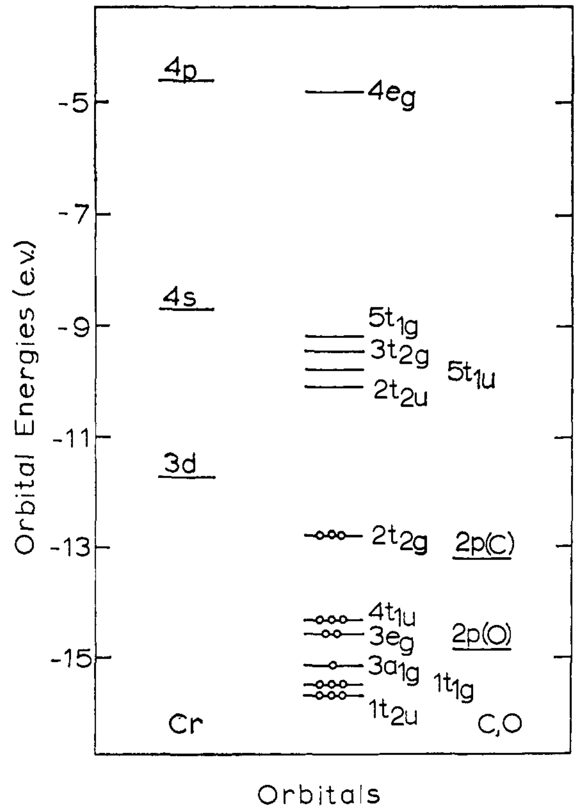

Figure 4. Partial molecular orbital energy level diagram for $Cr(CO)_6$. Circles represent electron pairs.

charge (1.90) of titanium also compares well with the charge (1.92) derived from the more complete calculation.

A partial energy level diagram for $Ni(CO)_4$ is depicted in Figure 2. Figure 3 displays a comparison of the experimental and calculated electronic spectra of $Ni(CO)_4$ and Table XI contains the data related to the intensities of the symmetry-allowed transitions. Figure 2 shows that the highest occupied and lowest unoccupied MO's are $5t_2$ and 3e, respectively. The filled 2e level is very close to and slightly more stable than the $5t_2$ level. The electronic transitions up to *ca.* 6.5 eV in $Ni(CO)_4$ are clearly metal-to-ligand in character. Except for an over-large spread in the energy scale, the gross features of the spectrum are quite well reproduced by this MO model. It is evident that the electronic spectrum results from a number of allowed transitions.

Table XI. Calculated Electronic Absorption Spectrum of $Ni(CO)_4$

Energy of obsd band max, eV	Transition Type	Orbital energy dif, eV	"Intensity"[a] $\nu \vert M \vert^2/e^2$
6.02	$4t_2 \longrightarrow 6t_2$	6.15	2.49
	$4t_2 \longrightarrow 3e$	5.79	0.70
5.52	$2e \longrightarrow 2t_1$	3.69	0.264
	$5t_2 \longrightarrow 2t_1$	3.64	0.551
5.24	$2e \longrightarrow 6t_2$	3.09	0.187
	$5t_2 \longrightarrow 6t_2$	3.04	0.226
	$5t_2 \longrightarrow 3e$	2.68	0.368

[a] Since only relative band intensities are of interest, the variable part, $\nu D = \nu |M|^2/e^2$, of the oscillator strength, $f = (8\pi^2 m_e c/3h)\nu D$, is used. D is in units of length^2 and, therefore, $|M|^2(e^2 \times \text{length}^2)$ is divided by e^2. The differences of one-electron orbital energies (eV) are employed for ν. Therefore, $\nu|M|^2/e^2$ is in units of eV Å^2.

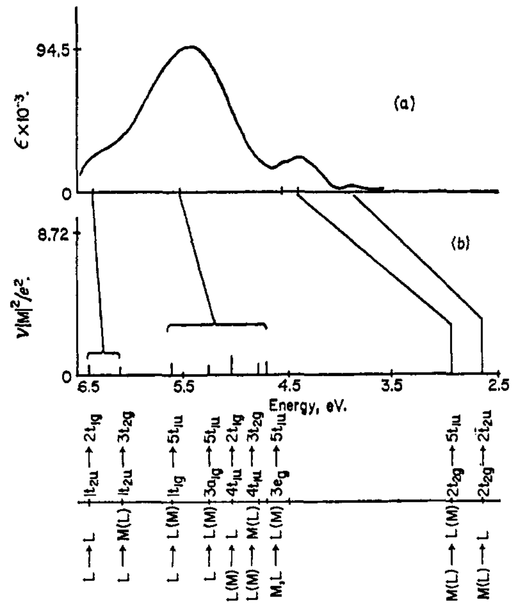

Figure 5. Experimental (a) and calculated (b) electronic spectra for $Cr(CO)_6$. See Figure 3 caption for notation.

A partial energy level diagram of $Cr(CO)_6$ is depicted in Figure 4. Figure 5 displays a comparison of the experimental and calculated electronic spectra of this molecule, and Table XII lists other relevant data. The energy level diagram obtained for $Cr(CO)_6$ is significantly different from that proposed on the basis of a more qualitative method of estimating energy levels of the basis set orbitals.[33] In particular, assignment of the low-intensity low-energy absorption as a $t_{2g} \rightarrow e_g$ transition seems out of the question on the basis of the present results. This conclusion has also been reported elsewhere.[34] There are several other differences between the present results and the earlier work. It appears that the lowest allowed transitions are largely metal-to-ligand in character. The most intense band (or bands) is probably due to a number of transitions,

Table XII. Calculated Electronic Absorption Spectrum of $Cr(CO)_6$

Energy of obsd band max, eV	Transition Type and orbital energy dif, eV	"Intensity" $\nu \vert M \vert^2/e^2$
6.35	$1t_{2u} \longrightarrow 2t_{1g}$ 6.38	0.44
	$1t_{2u} \longrightarrow 3t_{2g}$ 6.08	0.307
5.52	$1t_{1g} \longrightarrow 5t_{1u}$ 5.6	0.855
	$3a_{1g} \longrightarrow 5t_{1u}$ 5.25	0.635
	$4t_{1u} \longrightarrow 2t_{1g}$ 5.06	1.18
	$4t_{1u} \longrightarrow 3t_{2g}$ 4.78	0.717
	$3e_g \longrightarrow 5t_{1u}$ 4.7	0.818
4.59	$3e_g \longrightarrow 3t_{2g}$ 5.0	0
4.43	$2t_{2g} \longrightarrow 5t_{1u}$ 2.95	3.33
3.89	$2t_{2g} \longrightarrow 2t_{2u}$ 2.65	3.51

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(33) H. B. Gray and N. H. Beach, *J. Am. Chem. Soc.*, **85**, 2922 (1963).

(34) M. I. Ban, S. Z. Fenyl, and M. Hegyhati, "Theory and Structure of Complex Compounds," B. Jezowska-Trzebiatowska, Ed., The Macmillan Co., New York, N. Y., 1964.

which are in part ligand-to-metal or which involve orbitals containing both metal and ligand character. The high-energy shoulder at about 6 eV is assigned to a ligand–ligand and/or ligand–metal transition.

From the partial MO diagram of $Fe(CO)_5$, low-energy metal-to-ligand transitions are expected, since unoccupied MO's with a_2' symmetry, which are purely ligand nonbonding orbitals, are energetically low lying.

Further commentary and comparison between calculated and observed electronic spectra must await more extensive experimental work. Experimental data on the electronic spectra of transition metal carbonyls are quite incomplete. There is as yet no work dealing with the low-temperature spectra, on the basis of which it might be possible to decide questions relating to vibronically allowed transitions.

The Structure of the *trans*-Dioxotetracyanomolybdate(IV) Ion in the Crystalline Salt $NaK_3MoO_2(CN)_4 \cdot 6H_2O$[1,2]

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Abstract: A three-dimensional X-ray analysis of structure for crystals conforming in preparative method, composition, and color to the classic specifications for a salt presumed to contain the eight-coordinate $Mo(OH)_4(CN)_4^{4-}$ ion demonstrates that the complexed species is in fact the octahedral *trans*-dioxotetracyanomolybdate(IV) ion, $MoO_2(CN)_4^{4-}$. These structural data and the recent study by Lippard and Russ together suggest that the $Mo(OH)_4(CN)_4^{4-}$ ion is not a stable species either in crystals or in solution. The orthorhombic unit cell of crystalline $NK_3MoO_2(CN)_4 \cdot 6H_2O$ has $a = 12.46$, $b = 7.16$, $c = 9.17$ Å, and contains two formula weights; the space group is Pmna-D_{2h}^7. Visually estimated cross-correlated intensities for 931 independent nonvanishing reflections recorded photographically with Mo $K\alpha$ radiation, approximately the number of data comprised in the Cu $K\alpha$ limiting sphere, were employed to determine structure; anisotropic full-matrix least-squares refinement led to $R = 0.078$. The red $MoO_2(CN)_4^{4-}$ ion, completely vulnerable to hydrolysis in solution, is stabilized in a quite remarkable crystalline arrangement that is suggestive of (1) a marked preference for uninhibited Mo=O double bonding in the complex anion and (2) a general mechanism whereby dehydrative hydrolysis of the crystal can occur. The complexing bond lengths, $Mo–C = 2.204 \pm 0.013$ and $Mo=O = 1.834 \pm 0.009$ Å, are each "anomalously" long for the type in an octahedral complex; it is pointed out that a significant lengthening of the equilibrium bond lengths is rationally concomitant with the concentration of excessively large resultant charge within an unduly limited volume.

Among the earlier investigations of the cyano complexes of quadrivalent and quinquevalent molybdenum, that of Bucknall and Wardlaw[5] in 1927 was both comprehensive and critical. Although they emphasized that the evidence developed during their study does not yield a unique formulation for the complex anion present in the red crystalline salt of empirical composition $4KCN \cdot MoO_2 \cdot 6H_2O$, most investigators, before and since, have favored the eight-coordinate formulation, $Mo(OH)_4(CN)_4^{4-}$, because the complex is readily derived from, or converted into, either of the octacyanomolybdate species, $Mo(CN)_8^{4-}$ or $Mo(CN)_8^{3-}$. On taking the red complex to be the $Mo(OH)_4(CN)_4^{4-}$ ion, it is then natural,[5] if by no means required, to write the blue hydrolytic product thereof as $Mo(OH)_3OH_2(CN)_4^{3-}$. Both species, if correctly formulated, would be especially pertinent to considerations of structure and bonding in discrete eight-coordination complexes.[6,7]

Quite recently, however, Lippard, *et al.*,[8,9] have presented a variety of persuasive, if somewhat indirect, evidence that the red complex present in the potassium and sodium salts is not the presumed $Mo(OH)_4(CN)_4^{4-}$ ion of the older literature, but is instead the *trans* form of the octahedral $MoO_2(CN)_4^{4-}$ ion. Our own X-ray examination of the potassium salt confirms the two-molecule monoclinic cell and the probable space group, $P2_1/c$-C_{2h}^5, reported by Lippard, *et al.*, and we agree that these data are incompatible with the existence in the crystal of $Mo(OH)_4(CN)_4^{4-}$ ions utilizing either of the coordination polyhedra that are known to be preferred for discrete eight-coordination.[7] The spectroscopic and other evidence which Lippard, *et al.*, educe in favor of the $MoO_2(CN)_4^{4-}$ formulation for the red complex (and of $MoO(OH)(CN)_4^{3-}$ for the blue species) need not be recapitulated here; we report instead a determination of structure for red orthorhombic crystals of a salt that is shown by our analysis to be correctly formulated as $NaK_3[MoO_2(CN)_4] \cdot 6H_2O$. Crystals of this mixed salt, identified as a minor impurity

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[2] Presented in part at the Summer Meeting of the American Crystallographic Association, Minneapolis, Minn., Aug 20–25, 1967, Abstract P5, and in the Symposium on Unusual Coordination Polyhedra, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 10–15, 1967.

[3] National Science Foundation Predoctoral Trainee, 1965–1968.

[4] Author to whom correspondence should be addressed.

[5] W. R. Bucknall and W. Wardlaw, *J. Chem. Soc.*, 2981 (1927), who cite numerous references to earlier work in this field.

[6] L. E. Orgel, *J. Inorg. Nucl. Chem.*, **14**, 136 (1960).

[7] J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, **2**, 235 (1963).

[8] S. J. Lippard, H. Nozaki, and B. J. Russ, *Chem. Commun.*, 118 (1967).

[9] S. J. Lippard and B. J. Russ, *Inorg. Chem.*, **6**, 1943 (1967).