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MOLECULAR ORBITAL THEORY FOR METAL COMPLEXES: FERROCYANIDE AND COBALTICYANIDE IONS

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A. INTRODUCTION

Since the initial proposal by Wolfsberg and Helmholz [1] for a simple method of estimating the off-diagonal elements of the Hamiltonian matrix, semi-empirical molecular orbital calculations have been applied to a variety [2–19] of inorganic complexes of the transition metals. For the most part, these calculations have been made on a particular complex with the intent of reproducing or assigning the electronic spectrum and discussing the bonding parameters (orbital populations, the nephelauxetic parameters β,[20] etc.) in species belonging to the cubic symmetry groups.

The theoretical justification for the initially *ad hoc* procedures[1] involved in such MO calculations rests in the SCF-LCAO-MO treatment of Roothaan[21] as modified by Richardson[22]. The particular method used here has been discussed in detail by Basch [4,23]; a criticism [24] and an alternative proposal[25] within the Richardson formulation have also been presented.

In the light of the semi-empirical nature of the calculation, an especially

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fruitful area of application would seem to be a series of complexes of the same ligand with different central metal ions where the empirical parameters are chosen from data on a well-understood member of the series; thus, in order that the calculation may hopefully yield correct values of parameters of interest (in this case eigenvalues of the energy levels), it is "normalized" by picking the F^σ, F^π, and diagonal energy elements of the ligand (here the cyanide ion) to reproduce the known levels of a model compound whose electronic spectrum is already assigned. Such a procedure has worked well in helping to explain spectra of the pentacyanonitrosyl complexes[5,6].

The two complexes chosen as model systems are the d^6 ferrocyanide $Fe(CN)_6^{4-}$ and cobalticyanide $Co(CN)_6^{3-}$ ions. Both, of course, are of O_h symmetry. Crystal structures reveal the following interatomic distances for $K_4Fe(CN)_6$ (Ref. 26) and $K_3Co(CN)_6 \cdot 3H_2O$ (Ref. 27):

Fe–C = 1.92 Å	Co–C = 1.89 Å
C–N = 1.16 Å	C–N = 1.15 Å

B. THE CALCULATION

In the complexes treated, the M–C distance was assumed to be 1.89 Å which is consistent with the only other structure data available, namely that for $Fe(CN)_6^{3-}$ (Ref. 28). The C–N distance seems to remain fairly constant for metal cyano compounds[29,30].

The metal 3d, 4s, and 4p orbitals together with two bonding σ levels, one π-bonding, and one π-antibonding level from each ligand span the manifold of the eigenvectors in our approximation. Metal radial functions are taken from the results of Richardson, *et al.*[31] and are given in Table 1. Cyanide ion wavefunctions were constructed by performing a Wolfsberg–Helmholz calculation together with P. T. Manoharan [32] and are also given in Table 1.

Using these functions, the group overlap matrix is calculated for metal orbitals and ligand combinations of appropriate symmetry[33]. Ligand–ligand overlap corrections to the group overlaps are considered according to the formulae given in Table 2. The results for $Fe(CN)_6^{4-}$ are given in Table 3. Having chosen the wavefunctions, we are left with the task of selecting proper values of the F-factors for approximating off-diagonal Hamiltonian elements as well as diagonal elements for the cyanide ion. F^π is fixed at 2.3 and F^σ is varied to fit the energy separation between the highest filled MO of t_{2g} symmetry and the first empty one of e_g symmetry at a value paralleling the energy of the first d → d band. More will be said on this point later.

TABLE 1

BASIS FUNCTIONS

Cobalt

$$\begin{aligned}
R(3d) &= 0.568\,\Phi_3(5.55)+0.606\,\Phi_3(2.10)\\
R(4s) &= -0.02047\,\Phi_1(26.375)+0.06920\,\Phi_2(10.175)\\
&\quad -0.1697\,\Phi_3(4.69)+1.0118\,\Phi_4(1.45)\\
R(4p) &= 0.04044\,\Phi_2(11.05)-0.13983\,\Phi_3(4.385)+1.00880\,\Phi_4(1.30)
\end{aligned}$$

Iron

$$\begin{aligned}
R(3d) &= 0.5505\,\Phi_3(5.35)+0.6206\,\Phi_3(2.00)\\
R(4s) &= -0.02078\,\Phi_1(25.38)+0.07052\,\Phi_2(9.75)\\
&\quad -0.1744\,\Phi_3(4.48)+1.0125\,\Phi_4(1.40)\\
R(4p) &= 0.01118\,\Phi_2(10.60)-0.03833\,\Phi_3(4.17)+1.00067\,\Phi_4(0.80)\\
\Phi_n(\mu) &= N_\mu r^{n-1}e^{-\mu r}
\end{aligned}$$

Cyanide MO's

$$\begin{aligned}
\psi(\sigma_1) &= 0.13941\,\Phi_{1sC}(5.2309)-0.00798\,\Phi_{1sN}(7.9690)\\
&\quad -0.14039\,\Phi_{2sC}(1.1678)-0.40478\,\Phi_{2sN}(1.8203)\\
&\quad -0.36192\,\Phi_{2pC}(1.2557)-0.11759\,\Phi_{2pC}(2.7262)\\
&\quad -0.12714\,\Phi_{1sN}(6.1186)+0.00851\,\Phi_{1sN}(8.9384)\\
&\quad +0.13699\,\Phi_{2sN}(1.3933)+0.33923\,\Phi_{2sN}(2.2216)\\
&\quad -0.49935\,\Phi_{2pN}(1.5058)-0.18072\,\Phi_{2pN}(3.2674)
\end{aligned}$$

$$\begin{aligned}
\psi(\sigma_2) &= -0.0943\,\Phi_{1sC}(5.2309)+0.0054\,\Phi_{1sC}(7.9690)\\
&\quad +0.0950\,\Phi_{2sC}(1.1678)+0.2738\,\Phi_{2sC}(1.8203)\\
&\quad +0.5613\,\Phi_{2pC}(1.2557)+0.1824\,\Phi_{2pC}(2.7262)\\
&\quad -0.0509\,\Phi_{1sN}(6.1186)+0.0034\,\Phi_{1sN}(8.9384)\\
&\quad +0.0547\,\Phi_{2sN}(1.3933)+0.1354\,\Phi_{2sN}(2.2216)\\
&\quad -0.5192\,\Phi_{2pN}(1.5058)-0.1879\,\Phi_{2pN}(3.2674)
\end{aligned}$$

$$\begin{aligned}
\psi(\pi^{b}) &= 0.4188\,\Phi_{2pC}(1.2557)+0.1361\,\Phi_{2pC}(2.7262)\\
&\quad +0.5388\,\Phi_{2pN}(1.5058)+0.1932\,\Phi_{2pN}(3.2674)
\end{aligned}$$

$$\begin{aligned}
\psi(\pi^{*}) &= 0.7535\,\Phi_{2pC}(1.2557)+0.2448\,\Phi_{2pC}(2.7262)\\
&\quad -0.6506\,\Phi_{2pN}(1.5058)-0.2354\,\Phi_{2pN}(3.2674)
\end{aligned}$$

C. ENERGY LEVELS OF THE CYANIDE ION

The HCN molecule is a natural starting point for consideration of appropriate experimental values of the CN^- anion energy levels; both in this molecule and in the octahedral transition metal complexes the anion levels are perturbed by the coulomb field of the adjacent positively-charged ion. The first ionization potential of HCN is reported[34] as 13.9 e.v. Since the highest filled σ level is undoubtedly stabilized by the proton field, the highest occupied level is the π-bonding one whose energy is consequently to be approximated by the ionization potential[35]; so $E_\pi = -113{,}000\ \text{cm}^{-1}$. The SCF molecular orbital calculations of McLean[36a] and Palke and Lipscomb[36b] quantitatively confirm this level ordering, namely, $\sigma < \pi$.

This state of affairs is, of course, in contrast to the one which prevails in the radical CN˙ where the ordering of the σ and π orbitals is inverted[37,38]. Just what the situation will be in regard to these levels in the complexes of interest in this

TABLE 2

LIGAND–LIGAND CORRECTIONS TO GROUP OVERLAPS

A_{1g}

$$G(4s, \sigma_{\text{comb.}}) = \frac{\sqrt{6}S(4s, \sigma)}{\sqrt{1+4S(\sigma, \sigma)_{cis}+S(\sigma, \sigma)_{trans}}}$$

$$G(\sigma_{1\text{comb.}}, \sigma_{2\text{comb.}}) = \frac{4S(\sigma_1, \sigma_2)_{cis}+S(\sigma_1, \sigma_2)_{trans}}{\sqrt{1+4S(\sigma_1, \sigma_1)_{cis}+S(\sigma_1, \sigma_1)_{trans}}\sqrt{1+4S(\sigma_2, \sigma_2)_{cis}+S(\sigma_2, \sigma_2)_{trans}}}$$

E_g

$$G(3d, \sigma_{\text{comb.}}) = \frac{\sqrt{3}S(3d, \sigma)}{\sqrt{1-2S(\sigma, \sigma)_{cis}+S(\sigma, \sigma)_{trans}}}$$

$$G(\sigma_{1\text{comb.}}, \sigma_{2\text{comb.}}) = \frac{S(\sigma_1, \sigma_2)_{trans}-2S(\sigma_1, \sigma_2)_{cis}}{\sqrt{1-2S(\sigma_1, \sigma_2)_{cis}+S(\sigma_1, \sigma_1)_{trans}}\sqrt{1-2S(\sigma_2, \sigma_2)_{cis}+S(\sigma_2, \sigma_2)_{trans}}}$$

T_{1g}

$$G(\pi_{\text{comb.}}, \pi^*{}_{\text{comb.}}) = \frac{-2S(\pi, \pi^*)_{cis}}{\sqrt{1-2S(\pi, \pi)_{cis}}\sqrt{1-2S(\pi^*, \pi^*)_{cis}}}$$

T_{1u}

$$G(4p, \sigma_{\text{comb.}}) = \frac{\sqrt{2}S(4p, \sigma)}{\sqrt{1-S(\sigma, \sigma)_{trans}}}$$

$$G(4p, \pi_{\text{comb.}}) = \frac{2S(4p, \pi)}{\sqrt{1+2S(\pi, \pi)_{cis}+S(\pi, \pi)_{trans}}}$$

$$G(\sigma_{1\text{comb.}}, \sigma_{2\text{comb.}}) = \frac{-S(\sigma_1, \sigma_2)_{trans}}{\sqrt{1-S(\sigma_1, \sigma_1)_{trans}}\sqrt{1-S(\sigma_2, \sigma_2)_{trans}}}$$

$$G(\pi_{\text{comb.}}, \pi^*{}_{\text{comb.}}) = \frac{2S(\pi, \pi^*)_{cis}+S(\pi, \pi^*)_{trans}}{\sqrt{1+2S(\pi, \pi)_{cis}+S(\pi, \pi)_{trans}}\sqrt{1+2S(\pi^*, \pi^*)_{cis}+S(\pi^*, \pi^*)_{trans}}}$$

$$G(\sigma_{\text{comb.}}, \pi_{\text{comb.}}) = \frac{2\sqrt{2}S(\sigma, \pi)_{cis}}{\sqrt{1-S(\sigma, \sigma)_{trans}}\sqrt{1+2S(\pi, \pi)_{cis}+S(\pi, \pi)_{trans}}}$$

T_{2u}

$$G(\pi_{\text{comb.}}, \pi^*{}_{\text{comb.}}) = \frac{S(\pi, \pi^*)_{cis}+2S(\pi, \pi^*)_{trans}}{\sqrt{1-S(\pi, \pi)_{cis}+2S(\pi, \pi)_{trans}}\sqrt{1+S(\pi^*, \pi^*)_{cis}+2S(\pi^*, \pi^*)_{trans}}}$$

TABLE 3

GROUP OVERLAP INTEGRALS FOR $Fe(CN)_6^{4-}$

A_{1g}

$G(4s, \sigma_{1\text{comb.}}) = -0.72986$

$G(4s, \sigma_{2\text{comb.}}) = 0.55464$

$G(\sigma_{1\text{comb.}}, \sigma_{2\text{comb.}}) = -0.30471$

E_g

$G(3d, \sigma_{1\text{comb.}}) = -0.31305$

$G(3d, \sigma_{2\text{comb.}}) = 0.24386$

$G(\sigma_{1\text{comb.}}, \sigma_{2\text{comb.}}) = 0.11117$

T_{1g}

$G(\pi_{\text{comb.}}, \pi^*{}_{\text{comb.}}) = 0.06874$

T_{1u}

$G(4p, \sigma_{1\text{comb.}}) = -0.17271$

$G(4p, \sigma_{2\text{comb.}}) = 0.13462$

$G(4p, \pi_{\text{comb.}}) = 0.37559$

$G(4p, \pi^*{}_{\text{comb.}}) = -0.30434$

$G(\sigma_{1\text{comb.}}, \sigma_{2\text{comb.}}) = -0.00522$

$G(\pi_{\text{comb.}}, \pi^*{}_{\text{comb.}}) = -0.06986$

$G(\sigma_{1\text{comb.}}, \pi_{\text{comb.}}) = -0.05279$

$G(\sigma_{1\text{comb.}}, \pi^*{}_{\text{comb.}}) = 0.07565$

$G(\sigma_{2\text{comb.}}, \pi_{\text{comb.}}) = 0.04247$

$G(\sigma_{2\text{comb.}}, \pi^*{}_{\text{comb.}}) = -0.07032$

T_{2u}

$G(\pi_{\text{comb.}}, \pi^*{}_{\text{comb.}}) = 0.06874$

work depends on the coulomb field which the cyanide "sees"; due to the smaller positive charge which remains on the metal after complexation and the presence of other negatively charged ions in close proximity, the σ orbital may be destabilized from its position in HCN; in this case, the electronic configuration of cyanide would be obtained *simply* by placing an additional electron in the most stable, unfilled level of $\mathrm{CN}^{\cdot}$ giving $KK(z\sigma)^2(y\sigma)^2(w\pi)^4(x\sigma)^2:{}^1\Sigma$.

Assuming for the moment that this is indeed the case, the other diatomic energy levels may be estimated easily. Herzberg[39] reports the transition ${}^2\Sigma^+ \rightarrow {}^2\Pi_i$ *ca.* 9000 cm^{-1} and ${}^2\Sigma^+ \rightarrow {}^2\Sigma^+$ *ca.* 25,000 cm^{-1} in $\mathrm{CN}^{\cdot}$. The former may be assigned the configurations $\ldots(w\pi)^4(x\sigma) \rightarrow \ldots(w\pi)^3(x\sigma)^2$ and fixes the $x\sigma$ level at 9000 cm^{-1} higher energy than $w\pi$; if $w\pi$ is kept at the reasonable value of $-113{,}000$ cm^{-1}, this highest occupied σ orbital is at $-104{,}000$ cm^{-1}. The transition ${}^2\Sigma^+ \rightarrow {}^2\Sigma^+$ results from the process $\ldots(y\sigma)^2(w\pi)^4(x\sigma) \rightarrow (y\sigma)(w\pi)^4(x\sigma)^2$; Radford[40] reached this same conclusion on the basis of hyperfine structure of $B\Sigma^+$. By a similar line of reasoning this gives the $y\sigma$ energy as $-129{,}000$ cm^{-1}.

Using the calculations of Iguchi[41], it has been estimated[42] that the $v\pi$ level in cyanide complexes is around $-35{,}000$ cm^{-1}. No complete experimental evidence is available on this point. Carroll[43] believes that the observed states $E^2\Sigma$ and $J^2\Delta$ at *ca.* 60,000 cm^{-1} arise from the configuration $\ldots(y\sigma)^2(w\pi)^3(x\sigma)(v\pi)$; unfortunately, the other seven states predicted from the configuration have not been observed. Thus, a reliable estimate of the $v\pi$ energy from an average of state energies cannot be obtained.

We are left, then, with two ambiguities which are unresolved by our appeal to empirical data, namely: the level ordering of $x\sigma$ and $w\pi$; and the energy of the $v\pi$ orbital. For our purposes, these matters were resolved by calculations on the model compounds ferrocyanide and cobalticyanide. It was found as indicated above that the spectra of these complexes were most adequately represented by the calculation when the order of stability was taken as $\pi < \sigma$. Molecular orbitals for the cyanide ion were calculated using Roothaans's programs[44] to have the energy ordering proposed here. Using data given by Walsh[45], the position of $v\pi$ in the model molecule HCN is placed at *ca.* $-40{,}000$ cm^{-1}. Also, the energy value for $v\pi$ in the complexes was found to be best given as $-40{,}000$ cm^{-1}. The energies of the cyanide orbitals are set out in Table 4.

Henceforth, we shall refer to $w\pi$ as π^b, the bonding π-orbital and $v\pi$ as π^*,

TABLE 4

ENERGIES OF THE CYANIDE AND IRON ORBITALS

Cyanide orbitals		*Iron orbitals*	
σ_1	$-125{,}000$ cm^{-1}	3d	$-104{,}280$
π^b	$-113{,}000$	4s	$-83{,}540$
σ_2	$-104{,}000$	4p	$-46{,}310$
π^*	$-40{,}000$		

the antibonding π-orbital, the w-, v-nomenclature being primarily suitable for discussion of simple diatomics.

Metal orbital energies are estimated from Moore's tables[46] as functions of charge and configuration. The Hamiltonian matrix for an assumed metal charge and configuration is computed, the secular equations are solved, and finally the whole calculation is iterated to self-consistency by use of an IBM 7094 program.

D. POPULATION ANALYSIS

The criterion for self-consistency is, of course, the gross atomic charge and atomic orbital populations of the metal ion; Richardson's theory[22] and previous applications[12–19] have assumed that these quantities were given by the Mulliken[47] method of distributing MO populations over the participating atomic basis orbitals, namely, that the overlap population was to be divided equally between the two orbitals concerned.

Our results showed that, while this procedure gave adequate energy level schemes for first row hexacyano complexes, the gross population of the 4s metal orbital was predicted to be negative in analogous calculations of $Cr(CN)_6{}^{2-}$, $V(CN)_6{}^{3-}$, and $Ti(CN)_6{}^{3-}$. We interpret this physically meaningless result as an indication of very small or zero occupation. It is also to some degree an artifact of the calculation stemming from our inclusion of the σ_1 orbital of cyanide in the basis set. The electron density of this orbital is primarily localized between the C and N atoms, *i.e.*, it is the principal σ-bonding orbital of the anion; it thus turns out to have a negative overlap with metal 4s. When the (negative) overlap population is distributed equally between the two orbitals in the $1a_{1g}$ level (which is principally σ_1), the positive net atomic population on 4s is completely cancelled. Moreover, the participation of 4s in the filled $2a_{1g}$ level (which is principally σ_2) is not large enough to overshadow this effect.

Recognizing that any system of distributing overlap population is arbitrary, we have adopted the physically reasonable attitude that this quantity should be assigned to the atomic orbitals as fractions reflecting the relative importance of these basic functions in the molecular orbital. Representing a molecular orbital by $\Phi_i = a_i X_i + b_i Q_i$ where $Q_i = \Sigma_j C_{ij} \psi_j$ is a ligand symmetry orbital the overlap population is given by $2N_i a_i b_i \Sigma_j C_{ij} S_{ij}$ where N_i is the number of electrons in the occupied orbital; S_{ij} is the overlap integral and $\Sigma_j C_{ij} S_{ij} = G_i$ the group overlap integral. The fraction f_M assigned to the metal orbital is given by:

$$f_M = \frac{a_i{}^2}{a_i{}^2 + b_i{}^2}$$

and the fraction in the ligand symmetry orbital is:

$$f_L = \frac{b_i{}^2}{a_i{}^2 + b_i{}^2}$$

So instead of each orbital receiving $N_i a_i b_i G_i$ electrons, it receives $2f_A N_i a_i b_i G_i$ where $A = M, L$.

Fortunately, the results of the calculation seem to be fairly independent of the method used to divide charge. For example, using the Mulliken method for a calculation on $Fe(CN)_6^{4-}$ results in eigenvectors and energy separations not greatly different from those obtained with the method proposed here. A comparison is made in Table 5.

TABLE 5

RESULTS FOR TWO METHODS OF POPULATION DISTRIBUTION

$1a_{1g}$ *Eigenvector coefficients*			$e_g\sigma^* - t_{2g}\pi$ *Separation*	
Mulliken's method		*Our method*	*Mulliken's method*	*Our method*
4s	0.08738	0.12677	33,200 cm^{-1}	34,500 cm^{-1}
$\sigma_{1comb.}$	−0.82701	−0.80505		
$\sigma_{2comb.}$	0.24103	0.21961		

The gross atomic charge on the Fe, though, is increased from +0.23 to +0.43 by use of the square of coefficient proportionality factor. Such an effect is seen in all the first row complexes treated. The trends in metal charge and orbital population remain similar in both cases.

Note that this observation means that no significance is to be attached to the absolute values of charges and population predicted; these parameters are regarded as indicators that the self-consistent choice of orbital coefficients has been reached. Nevertheless, we may expect that *trends* in these quantities will be adequately reproduced if calculations are performed in an internally consistent fashion.

Although Richardson's treatment of the Hamiltonian matrix elements assumes that Mulliken's procedure is followed in population distribution, our method will not change the form of the equations, but will merely multiply inter-electronic potential terms by a constant f_A.

Also since it leads to a greater positive charge on the metal ion, the stability of metal orbitals will be enhanced; this is possibly one reason for the fact that values of F^σ are here found to be somewhat smaller (~1.50) for cyano complexes
Values of the diagonal metal Hamiltonian elements are given for the self-
than for halide complexes[4] where Mulliken's distribution was employed.
consistent result for $Fe(CN)_6^{4-}$ in Table 4.

E. ENERGY LEVELS AND EIGENVECTORS

Figure 1 presents the one-electron energy level scheme calculated for the ferrocyanide ion; a similar diagram is applicable to the $Co(CN)_6^{3-}$ ion as well.

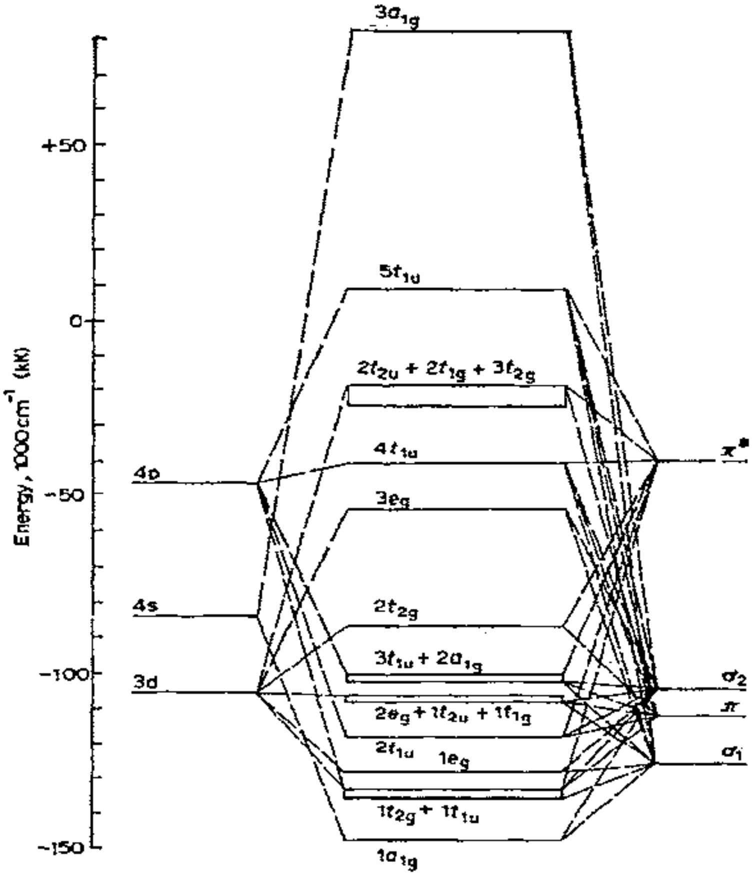

Fig. 1. Ferrocyanide energy levels.

The one electron energies for ferrocyanide are given in Table 6. Eigenvectors for $Fe(CN)_6^{4-}$ appear in Table 7, and eigenvalues and eigenvectors for $Co(CN)_6^{2-}$ are in Table 8.

TABLE 6

FERROCYANIDE ENERGY LEVELS

Level	*Energy (cm^{-1})*	*Level*	*Energy (cm^{-1})*
$1a_{1g}$	−147,700	$3t_{1u}$	−101,620
$1t_{2g}$	−135,900	$2t_{2g}$	− 87,960
$1t_{1u}$	−133,000	$3e_g$	− 53,420
$1e_g$	−129,350	$4t_{1u}$	− 41,070
$2t_{1u}$	−117,900	$2t_{2u}$	− 34,950
$2e_g$	−108,480	$2t_{1g}$	− 31,140
$1t_{2u}$	−107,050	$3t_{2g}$	− 31,080
$1t_{1g}$	−106,880	$5t_{1u}$	+ 9,450
$2a_{1g}$	−102,280	$3a_{1g}$	+ 77,870

TABLE 7

FERROCYANIDE EIGENVECTORS

Level	3d	4s	4p	σ_1	σ_2	π	π^*
$1a_{1g}$		0.12677		−0.80505	0.21961		
$1t_{2g}$	0.49313					0.77708	−0.05791
$1t_{1u}$			0.10115	−0.78568	0.07140	0.49297	−0.04648
$1e_g$	0.45658			−0.75856	−0.02483		
$2t_{1u}$			−0.20826	−0.61414	−0.26611	−0.67885	−0.01429
$2e_g$	−0.44371			−0.33940	−0.75046		
$1t_{2u}$						0.99323	0.06645
$1t_{1g}$						0.97915	0.11590
$2a_{1g}$		−0.28746		0.54455	1.02620		
$3t_{1u}$			0.11330	0.12147	−0.96141	0.28135	0.06337
$2t_{2g}$	−0.77286					0.64164	0.27701
$3e_g$	0.89954			0.68262	−0.73851		
$4t_{1u}$			0.25977	−0.13228	0.13298	0.26130	0.90540
$2t_{2u}$						−0.13505	1.00020
$2t_{1g}$						−0.23774	1.00090
$3t_{2g}$	0.49972					−0.12166	0.99048
$5t_{1u}$			1.09270	0.07583	−0.05018	−0.56226	0.52959
$3a_{1g}$		1.69600		1.12410	−0.62383		

Ligands contribute a total of 48 electrons which, when placed in the energy levels, fill all levels up through $3t_{1u}$. The d electrons of the metal ion are then to be accommodated in the $2t_{2g}$ level for all d^n configurations where $n \leq 6$ in the strong field cyanide complexes. Six d-electrons exactly fill the t_{2g} level; the first empty MO is predicted to be of e_g symmetry. Crystal field theory, of course, makes a similar prediction, namely, that in an octahedral crystal field the metal d-electrons

TABLE 8

RESULTS FOR $Co(CN)_6^{3-}$ COEFFICIENTS

Level	*Energy (cm⁻¹)*	3d	4s	4p	σ_1	σ_2	π	π^*
$1a_{1g}$	−149,890		0.15264		−0.78439	0.21150		
$1t_{2g}$	−136,160	0.56999					0.72590	−0.06801
$1t_{1u}$	−132,690			0.11723	−0.76391	0.07111	0.50568	0.44345
$1e_g$	−131,010	0.56743			−0.67647	0.02776		
$2t_{1u}$	−117,500			0.21055	0.64240	0.25516	0.66456	0.01712
$2e_g$	−109,840	0.43674			0.46963	0.70111		
$1t_{2u}$	−107,050						0.99323	0.06645
$1t_{1g}$	−106,890						0.97915	0.11590
$2a_{1g}$	−104,260		−0.01865		0.55517	1.02160		
$3t_{1u}$	−100,560			0.10798	0.12422	−0.96422	0.27614	0.06487
$2t_{2g}$	−94,230	−0.75800					0.70063	0.20306
$3e_g$	−59,340	0.81285			0.66942	−0.77537		
$4t_{1u}$	−40,980			−0.25962	−0.14249	0.13862	0.26597	0.90224
$2t_{2u}$	−34,960						−0.13505	1.00020
$3t_{2g}$	−33,810	0.40975					−0.07205	1.00060
$2t_{1g}$	−31,140						−0.23774	1.00090
$5t_{1u}$	+15,140			1.11380	0.11877	−0.06797	−0.57839	0.54748
$3a_{1g}$	+109,360		1.78990		1.20250	−0.70508		

occupy pure d-orbitals whose degeneracy is lifted to give a t_{2g} set and an e_g set having an energy separation $\Delta \equiv 10\ Dq$.

From crystal field considerations, the Δ value of ferrocyanide is known[42] to be $\sim$33,800 cm^{-1}; the calculated separation between $2t_{2g}$ and $3e_g$ is 34,500 cm^{-1}. We do not, however, identify this quantity $E(3e_g)-E(2t_{2g})$ with Δ for the following reason: Δ is defined as purely a one-electron quantity while the energy separation calculated here for levels which are mixtures of metal d-orbitals and ligand orbitals is a badly defined mixture of one- and two-electron integrals[19,48]. The "calculated values of Δ" cannot be extracted easily from $E(3e_g)-E(2t_{2g})$ since by definition the interelectronic repulsion corrections used to calculate transition energies from Δ are different from those which must be applied to calculate transition energies from $E(3e_g)-E(2t_{2g})$.

Nevertheless, we do feel that it is reasonable to expect that the $3e_g-2t_{2g}$ energy separation should follow the trends of the first ligand field band of the complex. Thus we have fit F^σ to cause the energy separation to correspond roughly to the first ligand field absorption band. This approach gives $F^\sigma = 1.50$ for $Co(CN)_6^{3-}$ and $F^\sigma = 1.53$ for $Fe(CN)_6^{4-}$.

F. ELECTRONIC SPECTRA OF d^6 SYSTEMS

Electronic spectra of several d^6 metal hexacyanide complexes are set out in Table 9. As has been noted[42] the fact that the $2t_{2g}$ level is completely filled in

TABLE 9

ELECTRONIC SPECTRA OF d^6 HEXACYANIDE IONS[a]

Ion	*Observed maxima (cm^{-1})*	$\varepsilon_{max.}$
$Fe(CN)_6^{4-}$	23,700	4.73
	31,000	302.0
	37,040 (sh)	~1000.0
	45,870	24,200.0
	50,000	23,700.0
$Ru(CN)_6^{4-}$ [c]	31,000	
	48,500	
	52,000	
$Os(CN)_6^{4-}$	47,000	47,400.0
	52,000	42,900.0
$Co(CN)_6^{3-}$	32,050	243.0
	38,460	180.0
	49,500	35,400.0
$Rh(CN)_6^{3-}$	30,800	13.7
	52,000 (sh)	9,780.0
	>52,000	
$Ir(CN)_6^{3-}$	35,100	7.52
	37,400	13.00
	>52,000	

[a] Solvent is water unless otherwise noted. [b] Nujol mull. [c] From ref. 42.

d^6 complexes leads to the expectation that only a few types of transitions can occur in the near IR, visible and UV regions, namely, components of the forbidden ligand field transition $t_{2g} \rightarrow e_g$ and the more intense, allowed metal-to-ligand charge transfer. The ferrocyanide spectrum shows a spin-allowed d→d band at 31,000 cm^{-1}, a weak shoulder at 37,040 cm^{-1} and two intense charge transfers at 45,870 and 50,000 cm^{-1}. Crystal field calculations give a value of ~34,000 for Δ while our MO results give a $2t_{2g} - 3e_g$ separation (which we label δ) of 34,500 cm^{-1}. Furthermore, the $2t_{2g} \rightarrow 4t_{1u}$ transition is predicted to fall at 46,900 cm^{-1} *vs.* the observed 45,870 cm^{-1}; the $2t_{2g} \rightarrow 2t_{2u}$ charge transfer is calculated at 53,000 cm^{-1} compared with the observed 50,000 cm^{-1}. In our scheme the predicted energies are not corrected for changes in interelectronic repulsion attendent on the transitions.

Aqueous solutions of $Co(CN)_6{}^{3-}$ exhibit ligand field transitions to ${}^1T_{1g}$ and ${}^1T_{2g}$ at 32,050 and 38,460 cm^{-1}, respectively, and the $t_{2g} \rightarrow t_{1u}$ M→L charge transfer at 49,500 cm^{-1}. The value of Δ is 34,800 cm^{-1}. Separation of $2t_{2g}$ and $3e_g$ is calculated at 34,500 while the charge transfer is predicted at 53,300 cm^{-1} which is, of course, also uncorrected for interelectronic repulsions.

Thus, it is apparent that the parameters F^{σ} and F^{π} as well as the value of the π^* energy may be selected in such a way as to give energy levels known from previous assignments. These assignments[42,49–51] are based on intensity data and semi-quantitative arguments; they are supported by our low-temperature measurements on these systems, which show that the bands assigned to orbitally forbidden transitions are in fact decreased in intensity.

G. POPULATIONS AND BACK-BONDING IN d^6

A good deal of infrared work[52–68] has been done in order to elucidate the nature of bonding in octahedral iron group cyanide complexes. The modes of principal interest in this regard are ν_6 the C≡N stretch and ν_9 the M–C stretch. Carbon to metal σ-bonding should tend to strengthen the M–C bond; metal to carbon π-bonding (back donation) should have the same effect[67,64]. Similarly, increased metal to carbon π-bonding as evidenced by enhanced population in the π^* ligand orbitals should decrease the C–N bond strength; metal–carbon σ-bonding increases the C–N bond order. These changes in bond strength are evidenced by changes in the force constants F_{M-C} and F_{C-N}. In situations where the modes can be assigned rather definitely to a particular motion (*i.e.* where Fermi resonance is small), these changes in F are paralleled by changes in the stretching frequencies observed for the bonds of interest. Computations indicate that this is the case for d^6 cyanide complexes[67].

Values of the stretching frequencies are given in Table 10 for d^6 complexes.

The calculated self consistent charge and orbital populations for ferrocyanide and cobalticyanide are:

$Fe^{+0.42}\, d^{7.05}\, s^{0.06}\, p^{0.47}$ $\sigma_1^{1.94}\, \pi^{1.97}\, \sigma_2^{1.73}\, \pi^{*0.07}$

$Co^{+0.41}\, d^{8.00}\, s^{0.09}\, p^{0.50}$ $\sigma_1^{1.89}\, \pi^{1.98}\, \sigma_2^{1.67}\, \pi^{*0.04}$

Although there is perhaps a slight exaggeration in the magnitude of the charge donated to Co^{III} as compared to Fe^{II}, the population trends are as predicted from the IR data, namely, Fe^{II} is seen to be a better back donor than Co^{III} as one might expect from oxidation state considerations; this is in line with the shift from 2129 cm^{-1} to 2044 cm^{-1} for the $C{\equiv}N$ anti-symmetric stretch in going from Co to Fe.

TABLE 10

VIBRATIONAL FREQUENCIES FOR d^6 HEXACYANIDES

Complex	ν_6 *(cm^{-1})*	ν_9 *(cm^{-1})*
$Co(CN)_6^{3-}$	$2129^{a,b}$	$416^{a,b}$
	2116^{c}	
	2118^{d}	414^{d}
$Fe(CN)_6^{4-}$	$2044^{a,b}$	$416^{a,b}$
	2026^{d}	414^{d}
$Rh(CN)_6^{3-}$	$2133^{a,b}$	$387^{a,b}$
	2107^{c}	
$Ru(CN)_6^{4-}$	2035^{d}	376
$Ir(CN)_6^{3-}$	$2130^{a,b}$	$401^{a,b}$
	2116^{c}	
$Os(CN)_6^{4-}$	2032^{d}	392^{d}

[a] From ref. 64. [b] In water. [c] This work; $CHCl_3$ solution. [d] B. M. CHADWICK AND A. G. SHARPE in *Advances in Inorganic Chemistry and Radiochemistry*, Academic Press, New York, 1966.

It seems, then, that understood trends in σ and π bonding are reproduced for d^6 by the calculation. Having thus demonstrated how the procedure is properly normalized, we may proceed to apply it to other hexacyano complexes. We note also that the same trends can, of course, be observed in experimental data for second and third row d^6 hexacyanides even allowing for the fact that not all the frequencies reported in Table 10 are observed in the same physical state. In cases where measurements are available for water solutions and chloroform solutions or solid mulls trends remain the same; the values of ν_6 in water seem shifted around 16 cm^{-1} to higher energies while ν_9 stays about constant compared with observations in $CHCl_3$ or solid. The differences between the M–C stretching frequencies in later rows point to a slight increase in bond strength in the order Rh^{III}–C > Ru^{II}–C and Ir^{III}–C > Os^{II}–C.

H. ELECTRONIC SPECTRA OF d^6 COMPLEXES OF THE SECOND AND THIRD ROW IONS

Other authors[42,51] have reported the spectra of the d^6 complexes $Ru(CN)_6^{4-}$ and $Os(CN)_6^{4-}$. We have measured the absorption of aqueous solutions of

$Rh(CN)_6^{3-}$ and $Ir(CN)_6^{3-}$. Rhodicyanide[69] displays a band at 30,800 cm^{-1} having $\varepsilon \sim 14$. We assign this as the $^1A_{1g} \rightarrow {}^3T_{1g}$ transition which, taking $C \sim 2400$ cm^{-1} would give $\Delta = 38{,}000$. The rather large intensity for a spin-forbidden band is to be expected in light of increased spin-orbit coupling in the second row[33] and is comparable to values observed for halide and ammine complexes of rhodium[70]. The intense shoulder at *ca.* 52,000 cm^{-1} is probably a component of the M→L $t_{2g} \rightarrow t_{1u}\pi^*$ excitation, its energy being increased over the analogous quantity in $Co(CN)_6^{3-}$.

Iridicyanide has two bands at 35,100 cm^{-1} and 37,400 cm^{-1} with ε's of 8 and 13, respectively. These are undoubtedly the $^1A_{1g} \rightarrow {}^3T_{1g}$ and $^1A_{1g} \rightarrow {}^3T_{2g}$ spin-forbidden transitions. Keeping $C \sim 2400$ (the presence of the lanthanide contraction does not allow us to anticipate further reduction of the Racah parameters in going from the second to the third row), we estimate $\Delta \sim 24{,}300$ cm^{-1}. The peak of the M→L charge transfer is not seen in this complex. From the shifts of the first M→L charge transfer in Fe–Ru–Os, the $t_{2g} \rightarrow t_{1u}\pi^*$ transition in Ir$^{\text{III}}$ might be anticipated between 50 kK and 52 kK. In all probability, the resolution prevents exact location of the band in $Ir(CN)_6^{3-}$; since the peak of the band $>53{,}000$ cm^{-1} cannot be seen, no meaningful Gaussian analysis is possible here.

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