A Comparison of Carbon Monoxide and Nitrogen as Ligands in Transition Metal Complexes

Kenneth G. Caulton, Roger L. DeKock, and Richard F. Fenske[1]

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. *Received June 26, 1969*

Abstract: The bonding characteristics of CO and N_2 in transition metal complexes are investigated on the basis of comparative molecular orbital calculations for $Cr(CO)_6$ and $Cr(N_2)_6$. The results suggest that the differences in π acceptor ability of the N_2 ligand compared to CO are consequences of the off-diagonal matrix element between the metal d orbitals and the π antibonding orbital of the ligand moieties. The σ bonding interactions can be mainly characterized as electron donation to the metal from orbitals substantially localized on the atoms adjacent to the metal. However, these orbitals have sufficient σ antibonding properties with respect to the ligand σ bond character that some degree of "within ligand" σ bond strengthening on complex formation cannot be ruled out. The results suggest that some of the apparent conflicts in π acceptor ability of the two ligands may be attributed to combined $\sigma-\pi$ factors.

There has been a recent surge of interest in the synthesis and study of transition metal complexes of molecular nitrogen.[2-7] Nitrogen was long thought to have no affinity for transition metals on the basis of the inertness of gaseous nitrogen itself, but it now seems that it was merely necessary to develop a sufficiently clever synthetic route to nitrogen complexes.

Along with the progress in synthetic routes to these complexes there has developed some disagreement as to the π acceptor ability of N_2 relative to CO. Thus, Collman, *et al.*,[5] claim on the basis of relative changes in N_2 and CO stretching frequencies in analogous compounds that "N_2 is a more powerful π acid than CO." In the same paper they also state that "Nitrogen is similar to NO^+ inasmuch as both are strong π acids and weak σ donors." Conversely, Bancroft, *et al.*,[6] state as a consequence of Mössbauer studies that "CO is an appreciably better σ donor and/or π acceptor than N_2."

From a theoretical standpoint, CO and N_2 are interesting ligand species. As free molecules, the calculated orbital energies of the two species[8] are surprisingly similar if one considers that the transfer of a proton from one nucleus to the other is involved in comparing the two isoelectronic molecules. Since N_2 forms complexes which are structurally similar[9,10] to those of CO, a comparison of the electronic structures of analogous complexes of CO and N_2 would be enlightening. Unfortunately the other ligands contained in known analogous species are of such complexity and the species are of such low molecular symmetry that theoretical computations are impossible without making severe simplifications in the calculations. Consequently, it was decided to undertake comparative calculations on the well-known compound, $Cr(CO)_6$, and the hypothetical molecule, $Cr(N_2)_6$. Not only does the high symmetry of this latter species make the calculations more tractable, but it permits one to focus attention on the bonding properties of N_2 relative to CO without the complexities introduced by the presence of other ligand species.

Calculational Method

Since the publication of the earlier results from this laboratory[11] for $Cr(CO)_6$, minor changes have been made in the computational method in order to simplify the calculational procedure. For example, recent investigations[12] have indicated that the three-center nuclear attraction integral can be very well approximated by

$$\left(\phi_a \left|\frac{q_v}{r_v}\right| \chi_b\right) \approx q_v \frac{S(\phi^a,\chi^b)}{2}\left[\frac{1}{R_{av}} + \frac{1}{R_{bv}}\right] \qquad (1)$$

where $S(\phi^a, \chi^b)$ is the overlap integral of the functions on centers a and b; q_v is the charge on center v, R_{av} and R_{bv} are the internuclear distances between the a and v centers and b and v centers, respectively.

The basis functions and internuclear distances for $Cr(CO)_6$ were the same as those used previously.[11] For purposes of comparison, the eigenvalues of the occupied orbitals obtained previously and in the present work are listed in Table I. The interpretations presented in our earlier communication[11] are completely unaffected by the small deviations in the eigenvalues listed in the table. As would be expected in the case of such close agreement, the eigenfunctions of the two sets of calculations are very similar as well.

In accord with the X-ray structural analysis[10] of $Ru(NH_3)_5N_2^{2+}$ which shows that the N_2 ligand bonds end-on through only one nitrogen, the calculations on the hypothetical $Cr(N_2)_6$ assumed a structure analogous to $Cr(CO)_6$. The chromium–carbon distance was set at the known distance of 1.92 Å.[13] The chromium–nitrogen distance was also taken as 1.92 Å so that a comparison of CO and N_2 as ligands would be unfettered by bond length changes. This invariance of Cr–N and Cr–C bond lengths is not incompatible with

(1) Author to whom reprint requests should be directed.
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Table I. Eigenvalues of Occupied Orbitals of $Cr(CO)_6$ and $Cr(N_2)_6$[a]

Orbital	$Cr(CO)_6$, previous work[b]	$Cr(CO)_6$, present work	$Cr(N_2)_6$, present work
$1a_{1g}$	−37.22	−38.00	−37.33
$2a_{1g}$	−18.51	−18.78	−21.31
$3a_{1g}$	−15.23	−17.28	−17.46
$1e_g$	−37.33	−38.79	−38.23
$2e_g$	−19.01	−19.37	−23.14
$3e_g$	−16.14	−17.42	−17.51
$1t_{1u}$	−37.21	−38.14	−37.39
$2t_{1u}$	−17.69	−17.35	−20.84
$3t_{1u}$	−14.97	−16.87	−17.47
$4t_{1u}$	−14.02	−15.24	−16.75
$1t_{2u}$	−14.95	−15.39	−16.83
$1t_{1g}$	−14.90	−15.36	−16.86
$1t_{2g}$	−16.24	−15.80	−17.10
$2t_{2g}$	−8.19	−8.30	−7.60

[a] In eV. [b] Reference 11.

orbital basis set used to carry out the calculations. The presentation of the eigenvectors in terms of ligand MO participation will aid in the discussion of the bonding characteristics of the species.

Even a cursory examination of the eigenvalues of $Cr(CO)_6$ and $Cr(N_2)_6$ given in Table I suggests that the stability of the former cannot be deduced on the basis of orbital energies. While the stability of a compound requires the consideration of many factors, such as the stability of the separated moieties, it is nevertheless somewhat surprising that the eigenvalues in the two cases are so similar.

It is informative to examine the stabilization of the metal $3d\pi$ orbitals as a consequence of interaction with the ligand 1π and 2π orbitals. Table IV summarizes the pertinent information. Notice that the quantity, $E(2t_{2g}) - F(3d\pi, 3d\pi)$, for $Cr(CO)_6$ is −2.49 eV, while its value for $Cr(N_2)_6$ is only −1.18 eV. Whether or not the $2t_{2g}$ level is higher or lower in energy than the diagonal matrix element, $F(3d\pi, 3d\pi)$, depends upon the competition between the $F(3d\pi, 1\pi)$ and $F(3d\pi, 2\pi)$ interactions. In $Cr(CO)_6$, these are −4.34 and −7.36 eV, respectively. However, the corresponding terms in $Cr(N_2)_6$ are −4.76 and −5.77 eV.

Table II. Eigenvectors and Eigenvalues of Occupied Orbitals of CO and N_2[a]

CO	2sC	2pσC	2sO	2pσO	2pπC	2pπO	Eigenvalue[b]	SCF eigenvalue[c]
3σ[d]	0.285	0.237	0.698	0.101			−38.60	−40.78
4σ	0.223	0.169	−0.485	0.813			−17.95	−19.93
5σ	0.785	−0.617	−0.070	−0.144			−14.63	−13.08
1π					0.494	0.752	−16.24	−15.86
2π[e]					0.909	−0.711	−1.32	7.09
N_2	$2sN_1$	$2p\sigma N_1$	$2sN_2$	$2p\sigma N_2$	$2p\pi N_1$	$2p\pi N_2$	Eigenvalue[b]	SCF eigenvalue[c]
$2\sigma_g$[d]	0.495	0.206	0.495	0.206			−36.30	−39.52
$2\sigma_u$	0.589	−0.398	−0.589	0.398			−17.42	−19.88
$3\sigma_g$	0.370	−0.614	0.370	−0.614			−16.46	−14.82
$1\pi_u$					0.624	0.624	−16.09	−15.77
$1\pi_g$[e]					0.835	−0.835	1.71	7.43

[a] The coordinate systems are such that σ overlap integrals are positive. [b] All eigenvalues are listed in units of eV. [c] SCF results are taken from ref 8. [d] Our method treated the 1s functions as part of the core. The orbital designation used here is in accord with the SCF results which treat the 1s functions as part of the basis set. [e] The 2π orbitals are unoccupied but are included here because of their significance in the bonding to the metal atom.

the X-ray diffraction results of Davis, Payne, and Ibers[14] on $Co(N_2)H[P(C_6H_5)_3]_3$, which showed that the observed Co–N_2 distance is similar to Co–CO distances in various cobalt carbonyl complexes. The nitrogen AO's and the nitrogen–nitrogen distance were the same as those used by Ransil[8] in his SCF calculation on N_2 using the Slater basis set.

Results and Discussion

Because they will be convenient for later discussion, the eigenvectors and eigenvalues of the free ligand species, CO and N_2, are given in Table II. These results are in reasonable accord with rigorous SCF values,[8] particularly when one considers the approximations involved in our calculational method. The results affirm the previously stated similarity in eigenvalues for the two species.

The eigenvalues for $Cr(CO)_6$ and $Cr(N_2)_6$ are presented in Table I. Since our previous work[11] tabulated the eigenvectors of $Cr(CO)_6$, which are essentially equivalent to those obtained in this work, only the $Cr(N_2)_6$ eigenvectors are tabulated in Table III. As with $Cr(CO)_6$, the eigenvectors of $Cr(N_2)_6$ are reported in terms of the free ligand basis functions, *i.e.*, the functions listed in Table II, rather than in terms of the atomic

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The reason for the reduction of $F(3d\pi, 2\pi)$ in the case of the nitrogen complex is apparent upon consideration of the form of the 2π ligand wavefunction and the resultant matrix element. A general form of the function is

$$\psi(2\pi) = c_1\phi_1 - c_2\phi_2 \tag{2}$$

in which the negative sign is consequence of the antibonding character of the function (see Table II); ϕ_1 is a normalized symmetry adapted linear combination of wave functions on those atoms adjacent to the chromium atom, and ϕ_2 is a similar set of functions on the more distant atoms. Expressed in this way, the coefficients, c_1 and c_2, can be taken directly from Table II. The matrix element then has the form

$$F(3d\pi, 2\pi) = c_1\langle 3d\pi|F|\phi_1\rangle - c_2\langle 3d\pi|F|\phi_2\rangle \tag{3}$$

Because of the greater proximity of atom one to the metal atom, $\langle 3d\pi|F|\phi_1\rangle$ will be larger than $\langle 3d\pi|F|\phi_2\rangle$ in both ligands. In free N_2, the two coefficients, c_1 and c_2, are identical and the total matrix element re-

Table III. Eigenvectors of Occupied Orbitals of $Cr(N_2)_6$ in a Basis of Free N_2 MO's

	3σ	4σ	5σ	6σ	4s		
$1a_{1g}$	1.0097	0.0234	0.0102	0.0015	−0.0552		
$2a_{1g}$	−0.0821	0.5828	0.4585	0.0201	0.2993		
$3a_{1g}$	−0.0042	−0.6808	0.7539	0.0054	0.0535		
	3σ	4σ	5σ	6σ	$3d\sigma$	$4d\sigma$	
$1e_g$	1.0643	0.0321	0.0001	−0.0056	−0.0108	−0.1648	
$2e_g$	−0.0613	0.5117	0.4962	0.0117	0.3855	0.1393	
$3e_g$	−0.0005	−0.6961	0.6968	−0.0046	0.0162	0.0338	
	1π	2π	$3d\pi$	$4d\pi$			
$1t_{2g}$	0.9757	0.0592	0.1519	−0.0634			
$2t_{2g}$	−0.3386	0.4774	0.7809	0.0635			
	3σ	4σ	5σ	6σ	1π	2π	4p
$1t_{1u}$	1.0272	0.0214	0.0047	−0.0019	−0.0095	−0.0037	−0.0843
$2t_{1u}$	−0.0660	0.6032	0.5019	0.0147	0.0417	−0.0075	0.3139
$3t_{1u}$	−0.0050	−0.6720	0.7385	0.0052	−0.0154	−0.0036	0.0502
$4t_{1u}$	0.0032	−0.0182	0.0497	−0.0020	1.0038	0.0376	0.0221
	1π	2π					
$1t_{2u}$	0.9993	0.0426					
$1t_{1g}$	1.0000	0.0417					

Table IV. T_{2g} Representation: Matrices,[a] $2t_{2g}$ Eigenfunctions, and Eigenvalues

	1π	2π	$3d\pi$	$4d\pi$
		F Matrix for $Cr(CO)_6$		
1π	−15.34	−1.22	−4.34	−3.05
2π		−2.34	−7.36	−5.48
$3d\pi$			−5.81	0.00
$4d\pi$				10.09
$\psi(2t_{2g}) = -0.34(1\pi) + 0.54(2\pi) + 0.69(3d\pi) + 0.04(4d\pi)$				
$E(2t_{2g}) = -8.30$ eV				
		F Matrix for $Cr(N_2)_6$		
1π	−16.71	−0.99	−4.76	−4.09
2π		−0.76	−5.77	−5.57
$3d\pi$			−6.42	0.00
$4d\pi$				9.42
$\psi(2t_{2g}) = -0.34(1\pi) + 0.48(2\pi) + 0.78(3d\pi) + 0.06(4d\pi)$				
$E(2t_{2g}) = -7.60$ eV				

[a] In units of eV.

Table V. Contributions to $F(3d\pi, 2\pi)$ in the T_{2g} Representation

	CO	N_2
c_1	0.909	0.835
c_2	0.711[a]	0.835[a]
$\langle 3d\pi\|F\|\phi_1\rangle$, eV	−8.27	−7.20
$\langle 3d\pi\|F\|\phi_2\rangle$, eV	−0.22	−0.31
$F(3d\pi, 2\pi)$, eV	−7.36	−5.77

[a] The sign in front of c_2 was changed from that listed in Table II to conform to eq 3.

flects the *difference* between $\langle 3d\pi|F|\phi_1\rangle$ and $\langle 3d\pi|F|\phi_2\rangle$. Since N_2 and CO are isoelectronic, the difference in the two molecules lies in the transfer of a proton from atom 1 to atom 2. Hence ϕ_1 on the carbon atom should be more diffuse while ϕ_2 on the oxygen becomes more contracted, which should increase the magnitude of $\langle 3d\pi|F|\phi_1\rangle$ and decrease $\langle 3d\pi|F|\phi_2\rangle$ in CO compared to N_2. Furthermore, in CO the c_1 coefficient is larger than c_2, 0.91 compared to 0.84. Both effects increase the first and decrease the second term in eq 3, which results in a substantial increase in the value of the total matrix element for CO. These qualitative arguments have also been considered by Jaffé and Orchin[15] and are now confirmed by the values given in Table V. The decreased $3d\pi$–2π interaction coupled with the greater separation of the $3d\pi$ and 2π diagonal matrix elements accounts for the decreased 2π and increased $3d\pi$ character in the $2t_{2g}$ molecular orbital for the $Cr(N_2)_6$ species.

In the results[11] on the isoelectronic series, $V(CO)_6^-$, $Cr(CO)_6$, and $Mn(CO)_6^+$, it was noted that the decreasing 2π participation in the $2t_{2g}$ molecular orbital was primarily a consequence of an increasing separation of the *diagonal* matrix elements. In this work, the difference in 2π interaction appears to be equally a function of the decreased value of the *off-diagonal* matrix element.

Parenthetically, it might be noted that while the method employed here results in a stabilization of the $2t_{2g}$ level, in accord with long held qualitative arguments,[16,17] more simplified calculational techniques such as the well-known SCCC method of Gray and coworkers,[18] which employ the Wolfsberg–Helmholz method for evaluation of $F(3d\pi, 1\pi)$ and $F(3d\pi, 2\pi)$ always appear to result in a destabilization of the level. This result occurs because the off-diagonal elements are estimated by

$$F(3d\pi, 1\pi) = K\cdot G(3d\pi, 1\pi)[F(3d\pi, 3d\pi) + F(1\pi, 1\pi)]/2 \quad (4a)$$

and

$$F(3d\pi, 2\pi) = K\cdot G(3d\pi, 2\pi)[F(3d\pi, 3d\pi) + F(2\pi, 2\pi)]/2 \quad (4b)$$

where $G(i, j)$ is the group overlap integral, K is a factor (sometimes a function of $G(i, j)$) often set equal to 2.0. The values used for $F(1\pi, 1\pi)$ are so much greater than those used for $F(2\pi, 2\pi)$ that the matrix element $F(3d\pi, 1\pi)$ is substantially larger than $F(3d\pi, 2\pi)$, causing the destabilization. Such a result appears to be

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Table VI. Electron Distribution in $Cr(CO)_6$ and $Cr(N_2)_6$

	3d(t_{2g})	3d(e_g)	4s	4p	4d	3σ	4σ	5σ	6σ	1π	2π
$Cr(CO)_6$	3.57	1.50	0.43	1.45	−0.05	2.00[a]	2.00	1.38	0.00	4.00[b]	0.42[b]
$Cr(N_2)_6$	4.12	1.07	0.47	1.28	−0.01	2.00[a]	1.74	1.72	0.00	4.00[b]	0.32[b]

For $Cr(N_2)_6$: $\theta_4 = (1/\sqrt{2})(4\sigma - 5\sigma)$ population = 2.00
$\theta_5 = (1/\sqrt{2})(4\sigma + 5\sigma)$ population = 1.46

[a] The ligand values are those for a single CO or N_2 group. [b] The maximum occupancy of a σ orbital is 2.00 electrons. The π orbital values given here take into account the double degeneracy of the π interactions.

an artifact of the calculational method which has doubtful validity.

Bonding Characteristics

Electron Distribution. As in previous work in this laboratory, the computations were carried to self-consistency of charge and electron populations on the various atoms *via* a Mulliken population analysis.[19] Similar calculations were carried out with the Löwdin[20] method for electron distribution. While the absolute values varied in the two cases, as expected,[21] the general trends in distributions between the two molecules were the same. Since much of the previous work is reported in terms of the Mulliken method, it will be used here as well.

It is worthwhile to represent the ligand charge distributions in terms of the ligand *molecular* orbitals rather than the individual *atomic* orbitals. The charge distributions are presented in Table VI. The trends are indicative on several counts.

If one were to envision a crystal field model for the metal atom configuration, it would be $(t_{2g})^6e_g^0$. The decrease in the t_{2g} occupation then becomes an estimate of the ability of the metal–ligand π interaction to transfer charge to the ligands. Conversely, the increase of density within the e_g metal orbitals estimates the σ bonding donation from the ligands to the metal. (These arguments represent a somewhat simplified view which ignores the complexity introduced by the 4p orbitals which are capable of both σ and π interaction.) The smaller t_{2g} and larger e_g metal orbital populations for $Cr(CO)_6$ clearly indicate the better σ and π interaction of $Cr(CO)_6$ compared to $Cr(N_2)_6$, and display the mutual enhancement of these interactions *via* the synergic effect. Notice that it is the orbital occupancy which differs much more dramatically than the total 3d populations.

The electron populations in the 1π ligand orbitals indicate that any π donating effect by this orbital through, for example, the $1t_{2g}$ molecular orbitals is counterbalanced by back donation, so that the 1π occupation is unchanged from that of the free ligand. The significant π interaction, of course, involves the 2π ligand orbitals which accept electron density *via* interaction with the filled metal $3d\pi$ orbitals. The larger 2π occupation for $Cr(CO)_6$ than for $Cr(N_2)_6$ is in keeping with the $3d\pi$ occupancy previously mentioned.

One interesting result appears upon examination of the ligand populations in the 4σ and 5σ orbitals. These two orbitals are completely filled in the free ligands. In $Cr(CO)_6$, the σ donation to the metal occurs *via* the 5σ orbital, while in $Cr(N_2)_6$, both the 4σ and 5σ are involved to approximately the same extent. From Table II, one sees that the 5σ orbital in CO is substantially localized on the carbon atom. In the N_2 complex, the 4σ and 5σ orbitals (labeled $2\sigma_u$ and $3\sigma_g$ in Table II) are, by the choice of basis set, delocalized over the N_2 molecule. However, if one takes linear combinations of the two functions

$$\begin{aligned}\theta_4 &= (1/\sqrt{2})(4\sigma - 5\sigma) = (1/\sqrt{2})(2\sigma_u - 3\sigma_g)\\ \theta_5 &= (1/\sqrt{2})(4\sigma + 5\sigma) = (1/\sqrt{2})(2\sigma_u + 3\sigma_g)\end{aligned} \quad (5)$$

then these two new functions are again essentially localized on nitrogen atoms 2 and 1, respectively. Their populations are also listed in Table VI and clearly indicate that, as in the carbonyl complex, the σ donation to the metal comes essentially from the atom adjacent to the metal. The values of 1.38 for 5σ on CO and 1.46 for θ_5 on N_2 again illustrate the weaker σ donating ability of the N_2 group in these complexes.

While the substantially localized character of the 5σ orbital in CO and the θ_5 orbital in N_2 aid in correlating the MO results with a valence bond localized orbital interaction, it is important to keep in mind that the two orbitals are slightly *antibonding* with respect to the σ framework of the two ligand species. Thus, the 5σ orbital of free CO has a negative overlap population, −0.047, as does θ_5 in N_2, −0.036. Removal of electron density from these orbitals results in an increase in σ bond strength for their respective molecules. Therefore, although π bond strength in the CO complex is reduced to a greater degree than that in the N_2 complex, there is a greater σ bond strengthening in the CO complex, since a greater portion of electron density was removed from the 5σ orbital, and the orbital possesses a larger antibonding character than the θ_5 function.

It is clear, then, that the resultant bond strength in the two ligand species compared to their strengths as free ligands is not necessarily relatable to π interaction only. Since such characteristics as stretching frequencies will depend on total bond strength, the π interactions cannot be isolated from potential σ effects. It is possible that some of the controversy over relative π acceptor abilities of these ligands has resulted from failure to consider both changes. Furthermore, the balance between σ bond strengthening and π bond weakening suggests that the final bond character in mixed-ligand complexes could be dependent upon the nature of the other attached ligands. It is the suggestion of the authors that the properties of CO and N_2 in ML_5X (where X = CO or N_2) will depend upon the ligand L. Future work in this laboratory will include efforts to verify this conjecture.

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