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Bonding and Frequency Shifts in XN_2 and XCO Compounds

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Received June 20, 1969

The origin of the general experimental observation that $\Delta F_{N_2} > \Delta F_{CO}$ for N_2 vs. XN_2 and CO vs. XCO is discussed. The relative donor-acceptor properties of N_2 and CO are examined in general terms applicable to a wide range of π donor substituents, X. Specific examples, for illustrative purposes, are $X = N^-$ and O. These simple substituted N_2 and CO compounds have been treated by rigorous SCF procedures and those results form a quantitative basis for the discussion.

Introduction

Recent developments in the field of synthetic coordination chemistry have led to the preparation of several complexes containing molecular nitrogen, N_2.[1] Those structures which have been determined[2] reveal the linear MNN arrangement (M = metal atom) which is commonly observed for the 10 valence electron donors CN^-, CO, and NO^+. The mode of attachment of N_2 to M is now a question of some concern, and, in particular, the pi acceptor ability of N_2, relative to CO, is under scrutiny. The convenient experimental quantity for estimating the π^* acceptor property of N_2 is the force constant change on complex formation. For analogous CO and N_2 complexes it has been pointed out[1b] that $\Delta\nu_{N_2}$ is greater than $\Delta\nu_{CO}$. One interpretation[1b] of this is that N_2 is a better π^* acceptor than CO. This interpretation is, at least, unsettling in an intuitive sense. The purpose of this correspondence is to call attention to the results of recent « minimum basis, best atom » SCF calculations[3] for N_3^- and NCO^- which demonstrate the danger of inferring an order of π bonding for two ligands, such as N_2 and CO, from the relative order of N_2 and CO stretching frequency depressions on binding of these groups to the same substituent.

Unfortunately, reliable (for this purpose) LCAO—MO calculations on molecules as complex as $RhClL_2(N_2)$ and $RhClL_2(CO)$, $L = PPh_3$, are not feasible at this time. However, a comparison of the N_2 and CO stretching frequency (and force constant) depressions in NNN^- and NCO^- and ONN and OCO reveal that when N_2 and CO possess a common substituent, whether it be a complex fragment, N^-, or O, the order of $\Delta\nu_{N_2} > \Delta\nu_{CO}$ and $\Delta F_{N_2} > \Delta F_{CO}$ is found. This relative ordering of frequency depressions is, therefore, a very general phenomenon and is not intimately related to the nature of the substituent, as long as that substituent possesses occupied π symmetry orbitals. That the observed order is independent of the substituent, can only be taken to mean that the phenomenon results from basic differences in the occupied and virtual orbital structures of N_2 and CO. Since the explanation for this order of frequency depressions depends on the ligands and not on the substituent, insight into the source of this order may reasonably be obtained from a detailed study of NNN^- and NCO^-. Obviously, the magnitudes of force constant depressions are greater for the N^- and O substituents than for any conceivable transition metal complex; however, the experimental facts are that the order $\Delta\nu_{N_2} > \Delta\nu_{CO}$ is preserved over an extensive range of substituents.

Table I. [a]

	OCN^-	NNN^-
σ_d, e^-	1.00	0.74
π_a, e^-	−1.50	−1.26
$\sigma_d+\pi_a^*$, e^-	−0.50	−0.52
ΔF_{AB}, mdÅ^{-1}	−7.9 [b]	−9.3 [c]
Δn_t, e^-	−0.33	−0.38
Δn_σ, e^-	+0.16	+0.23
Δn_π, e^-	−0.49	−0.61

[a] All electron density quantities computed from the data in reference 3. [b] A. Maki and J. C. Decius, . *Chem. Phys.*, *31*, 772 (1959). [c] Computed from data in P. Gray and T. C. Waddington, *Trans. Faraday Soc.*, *53*, 901 (1957) and H. A. Papazian, *J. Chem. Phys.*, *34*, 1614 (1961).

The results, summarized in Table I in a form more useful for our purposes than in the original report,[3] allow several useful and interesting comparisons to be made. (In the table, σ_d = 6 minus the total gross populations[4] of the A and B $s+p_z$ atomic orbitals, π_a^* = 4 minus the A+B gross pπ ao densities, and $\sigma_d+\pi_a^*$ is the net change in diatom electron density). For example, N^- is a net electron donor in that considerably more electron density is back bon-

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(1) For a recent review of this area see (a) A. D. Allen and F. Bottomley, *Accts. Chem. Research*, *1*, 360 (1968); (b) J. P. Collman, M. Kubota, F. D. Vastine, J. Y. Sun, and J. W. Kang, *J. Am. Chem. Soc.*, *90*, 5430 (1968).

(2) J. H. Enemark, B. R. Davis, J. A. McGinnety, and J. A. Ibers, *Chem. Comm.*, *96* (1968), F. Bottemley and S. C. Nyburg, *Chem. Comm.*, 897 (1966).

(3) R. Bonaccorci, C. Petrongolo, E. Scrocco, and J. Tomasi, *J. Chem. Phys.* *48*, 1500 (1968).

(4) R. S. Mulliken, *J. Chem. Phys.*, *23*, 1833, 1841, 2338, 2343 (1955).

ded to CO and N_2 than is withdrawn from the CO and N_2 sigma orbitals.

It is important to note that a completely equivalent analysis of the σ donor and π^* acceptor properties of these ligands can always be given in terms of the free ligand orbitals as a basis set rather than individual a.o. basis functions.[5] When this is done, π^* occupation numbers, for example, are computed to be the same as determined here from the formula $\pi_a^* = 4$ minus the A+B gross $p\pi$ ao densities. A feature of this kind of analysis is that, again with respect to the π system, *both* the π and π^* orbitals of the ligand are delocalized or intimately mixed with substituent π orbitals. A degenerate pair of π_b orbitals (occupied) are delocalized over all three atoms but concentrated somewhat more on the central atom. The next higher energy pair is approximately non-bonding in that there is a node near the central atom (in the case of NNN^- and OCO, the node occurs precisely at this atomic position). The non-bonding orbital has large amplitudes, therefore, at the terminal atoms. These orbital characteristics are such that the diatom (*e.g.* N_2) π and π^* contributions to π_b reinforce at the central or donor atom and *cancel at this position* in π_n. The low amplitude of π_n at the central position contributes to the low negative or positive charge associated with central atom in compounds such as those considered in this report; the other contribution to low or positive charge at this position is the charge loss by this atom *via* its σ donor role. The same description is applicable to metal complexes, the differences between NN_2^- and NCO^- on the one hand and metal complexes on the other being ones of extent of substituent and diatom orbital mixing to form π_b, π_n, and π^*. This description is more closely linked to the concept of ligand polariaztion by the substituent but is in every way identical to that given above in terms of π_a^*.

The delocalization of both sigma and pi density reveals the extent of synergic charge flow on adduct formation. CO donates about 1/4 e^- more than N_2 and accepts about 1/4 e^- more. Therefore, and very significantly in a chemical sense, CO and N_2 are equally effective in removing charge density from the substituent.

N_2 and CO have the same total nuclear charge but this nuclear charge (and therefore the orbital densities) are differently distributed in the two molecules. To explain the CO, N_2 π^* acceptor order we note that the (virtual) π^* orbitals are evenly distributed between the N atoms of N_2 whereas the corresponding orbitals are more highly concentrated on the C of CO. This fact should give better overlap of substituent pi orbitals with $CO\pi^*$ than $N_2\pi^*$ and lead to greater delocalization of substituent pi density onto CO (alternately, greater mixing of $CO\pi^*$ into π_b and π_n). In addition, the $CO\pi^*$ orbital is computed[6] to lie at a slightly lower energy than that of N_2 which would also make the former the better acceptor orbital. The synergic relation between σ donation and π^* acceptance of electron density tends to further increase this disparity between $CO\pi^*$ and $N_2\pi^*$ as acceptor orbitals.

The computed change in diatom overlap populations, Δn_t, broken down onto $\sigma(\Delta n_\sigma)$ and $\pi(\Delta n_\pi)$ contributions, are given in the last three rows of Table I. With fair accuracy, we may expect to find a correlation between Δn_t and ΔF_{AB}.[4,7,8,9] The order of ΔF_{AB} and Δn_t are both found to be $CO < N_2$ (convincingly, the ratios of CO and N_2 Δn_t's = that of the ΔF's = 1.1). The order $\Delta F_{N_2} > \Delta F_{CO}$ is the same as the order $\Delta\nu N_2 > \Delta\nu_{CO}$ which is reported for analogous N_2 and CO complexes. These computations show that while CO is the better π^* acceptor, the decrease in CO and N_2 pi overlap popoulations are in the order $N_2 > CO$. One must be careful, however, in expecting the same proportionality between total pi density and pi overlap populations for two dissimilar diatom groupings. The pi overlap population of a homonuclear diatomic, with roughly the same internuclear distance as an isoelectronic heternuclear pair, will invariably be greater than that of the heteronuclear pair. The pi overlap population of N_2 is greater than that of CO. Conversely, the (virtual) π^* antibonding overlap population of N_2 is greater than that of CO (the π^* orbitals of N2 are more destabilizing to the N_2 link than those of CO are to the CO link); in the instance of equal population of CO and $N_2\pi^*$ orbitals the decrease in N_2 pi overlap population will be greater than that of CO. Such arguments account for the order, in Table I, of $\pi_a^*(N_2) < \pi_a^*(CO)$ but $\Delta n_\pi(N_2) > \Delta n_\pi(CO)$.

The SCF calculations, which should be quite accurate with respect to charge distribution, show the same trends in sigma donor and pi acceptor properties of N_2 and CO, reveal the operation of sigma-pi synergism, and agree with the experimental finding that $\Delta F_{N_2} > \Delta F_{CO}$ when these ligands bond N^- as expected when N_2 and CO coordinate a complex fragment such as $RhClL_2$.

Interpretation of the relative ΔF's in terms of sigma and pi covalent binding changes shows that the ΔF's cannot be assumed to be proportional to the π^* occupation numbers since $\pi_a^*(CO) > \pi_a^*(N_2)$. Furthermore, the changes in bond stiffness arise from both sigma and pi changes. For both N_2 and CO, the sigma overlap populations increase on binding N^-. The increase in sigma binding therefore opposes the decrease in pi overlap population in each case. In comparing N_2 with CO, $\delta(\Delta n_\sigma) = +0.07$ and $\delta(\Delta N_\pi) = -0.12$; the positive difference in Δn_σ's is not negligible and is responsible for bringing the relative Δn_t's to values consistent with the relative ΔF's. We note, however, that the Δn_σ, Δn_π order for any one of these ligands interacting with a pi donor substituent is $\Delta n_\sigma < \Delta n_\pi$, so that, within a series of related N2 compounds, it is entirely possible for ΔF_{N2} to closely follow the degree of $N_2\pi^*$ occupation.

The increase in σ overlap populations of these two diatoms on adduct formation is related to the role of

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[5] K. F. Purcell, *J. Am. Chem. Soc.*, *91*, 3487 (1969).

[6] B. J. Ransil, *Revs. Mod. Phys.*, 32, 245 (1960).

[7] A. F. Schreiner and T. L. Brown, *J. Am. Chem. Soc.*, *90*, 3366 (1968).

[8] K. G. Caulton and R. F. Fenske, *Inorg. Chem.*, *7*, 1273 (1968).

[9] K. F. Purcell, *J. Am. Chem. Soc.*, *89*, 6139 (1967).

the 4σ and 5σ (« lone pair ») orbitals.[4,5] In CO and N_2 these orbitals are « anti-bonding » in the sense that they have negative overlap populations;[4,10] the negative values of the $(4\sigma + 5\sigma)$ overlap populations reflect the repulsion expected from lone pair orbitals. On coordination, this repulsion is greatly reduced as a result of the attraction between one « lone pair » and the substituent nucleus. As a further consequence, the non-donor atom lone pair density will tend to be polarized into the binding region to replace charge drained from the σ orbitals of the donor atom.[5]

Acknowledgment. Is made to the donors of the Petroleum Research Fund administered by the American Chemical Society, for support of this research.

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(10) C. W. Scherr, *J. Chem. Phys.*, 23, 569 (1955).